EFFECTS OF PHYSICO-CHEMICAL PROPERTIES ON THE BULK ELECTRICAL CONDUCTIVITY OF TROPICAL SOILS

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DEDICATION

This thesis is dedicated to an esteem person, Dr. Yusuf N. Tamimi of Hawaii Branch Station, College of Tropical Agriculture and Human Resources, Hilo, for his valuable training, advice and patience with me during the years when I worked with him.

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INTRODUCTION

Soil salinization and soil erosion are the two major processes of land degradation. In arid areas where irrigation agriculture dominates, the problem of soil salinity becomes apparent. The endless global demand for food and other agricultural products to meet the requirement of the ever-growing population makes the study of soil resources, with particular regard to salt-affected soils, imperative and urgent. The lack of awareness and understanding of the processes leading to the formation of salt-affected soils inhibits their effective diagnosis and remedy. The unavailability of massive areas of such soils for sustained agricultural production is a serious burden to farmers' welfare and the world economy.

The major cause of the formation and occurrence of salt-affected soils is the accumulation of soluble salts, primarily Na ions in the solid and/or liquid-phase of the soil. The high Na content in the soil solid-phase (exchangeable Na) causes structural failure, colloidal dispersion, increased swelling and hydration and consequently results in unfavorable soil physical properties such as soil crusting, poor permeability, restricted drainage, etc. On the other hand, the high salt concentration in the soil liquid-phase is detrimental to plant growth by limiting the water uptake, inducing imbalances in nutrient uptake, metabolism and so on. Optimal crop production requires proper diagnosis, management and treatment of saline and sodic soils. Visual observations of the soil and growing plants often fail to identify and quantify the salinity or sodicity problem. The United States

Salinity Laboratory Staff (1954) reported that salinity might reduce crop yield as much as 25% without inducing visible symptoms. At the present time, the standard method of detecting soil salinity requires tests on soil samples that are brought into the laboratory. In some cases, a portable apparatus is used in the field to obtain less precise direct measurements of soil salinity (USSL, 1954; Bower, 1963). The standard method (saturation extract method) requires much time and effort especially when considering that soil salinity displays great spatial variability and has to be monitored periodically to reflect temperal variability. For this reason, a simple method for detecting soil salinity directly in the field without soil sampling, laboratory analysis and other complicated and time consuming procedures would be invaluable both for practical and research applications.

Since 1971, an alternate parameter, the Bulk Soil Electrical Conductivity, which is obtained by placing four equally spaced electrodes horizontally spanned over the soil surface, has been developed by the United States Salinity Laboratory workers to diagnose and quantify soil salinity. However, information concerning the effects of various soil, physical and chemical properties (including salt level, water content, exchangeable cations and soil bulk density) on bulk soil electrical conductivity is scarce. Most of the data obtained are based on experiments done on the U.S. Mainland (Halvorson and Rhoades, 1974; Rhoades, Raats and Prather, 1976). At the same time, the sugarcane, pineapple, and other irrigated agricultural industries in Hawaii are now experiencing increasing salinity problem. In light of these factors, there is a strong need to monitor salinity and sodicity in irrigated Hawaii soils and bulk soil electrical

conductivity needs to be developed as a reliable technique. Therefore the objectives of this study were:

1. To investigate the effect of salt level, water content, exchangeable cations and soil bulk density on bulk soil electrical conductivity (soil variables).

2. To evaluate the influence of soil particle-size distribution and mineralogy, through contributions to specific surface conductivity and dielectric properties on bulk soil electrical conductivity (inherent soil characteristics).

LITERATURE REVIEW

Terms and Definitions

a — Effective radius - The hypothetical equivalent radius of a sphere of a given material which would settle with the same velocity as the particle in question. It is evaluated by the following equation:

$$a = 3/P_p S$$

where P_p and S are the particle density and specific surface area (see below) of the mineral, respectively. It is expressed in cm.

CEC — Cation exchange capacity - The sum total of exchangeable cations that a soil can adsorb. It is expressed in meq/100gm of soil.

EC_a — Bulk soil electrical conductivity - The electrical conductivity of a segment of bulk soil determined by a 4-electrode technique (e.g. Wenner Array, see below). It is normally expressed in mmho/cm at 25°C.

EC_e — Electrical conductivity of saturation extract - The electrical conductivity of an extract from saturated soil measured by a D.C. Wheatstone-type Conductivity Bridge and an electrode cell. It is expressed in mmho/cm at 25°C.

ES_s — Specific surface conductivity - Assuming the solid-phase is made up of spherical particles, the specific surface conductivity of the solid-phase is defined as the following (Weiler and Chaussidon, 1966):

$$EC_s = 4\ K_s/a\pi$$

where K_s is the surface conductance (see below) in mho or mmho and "a" is the effective radius of the spherical particles. It is expressed in mho/cm or mmho/cm at 25°C.

EC_w Electrical conductivity of liquid-phase - The electrical conductivity of the soil solution as determined by a Wheatstone-type Conductivity Bridge and an electrode cell. It is expressed in mmho/cm at 25°C.

F Formation factor - A factor by which the solid-matrix reduces the electrical conductivity of the ambient (equilibrium) solution. In other words, it can be defined as the ratio of the conductivity of an equilibrium solution to that of a fictitious surficially inert medium (filled with that solution). It is dimensionless.

K_{iso} Iso-conductivity point - The electrical conductivity value at which the suspension's conductivity equals that of the supernatant. It is expressed in mmho/cm at 25°C.

K_s Surface conductance - The difference between the conductance of the suspension (gel) and that of the equilibrating solution is defined as the surface conductance. It is a measure of the product of the number of counter ions per unit area of the surface and the average mobility of these ions. It is expressed in mho or mmho at 25°C.

P_B Bulk density - The mass of dry soil per unit bulk volume. The bulk volume is determined before the soil is dried to constant weight at 105°C. It is expressed in gm/cm^3.

P_p Particle density - The mass per unit volume of the soil's solid-phase. It is expressed in gm/cm^3.

S Specific surface area - The surface area per unit mass of soil or mineral. It is expressed in m^2/gm or cm^2/gm of soil.

S_u Exposure density - The surface area of solid per unit volume of gel (suspension). It is expressed in cm^2/cm^3.

T Tortuosity or transmission coefficient - The reciprocal of the increase in diffusion path that an ion must take in diffusing through the water present in the soil when it moves along a concentration gradient or in response to the application of an electric current as compared to the path in free water. It is dimensionless.

Charge density - The excess of negative or positive charge per unit surface area of soil or mineral. It is evaluated by dividing the cation or anion exchange capacity by specific surface area of the soil or mineral. It is expressed in meq/cm^2 or esu/cm^2.

Wenner array - The horizontal arrangement along the soil surface of 4 electrodes for the purpose of measuring the soil electrical resistivity. The outer 2 electrodes are connected to a current source and the inner 2 to a resistance meter. The resistance across the inner pair of potential electrodes is measured while a constant current is passed between the outer pair of current electrodes.

The Theoretical Basis of the Dependence of Bulk Soil Electrical Conductivity on Soil Characteristics

Most soil constituents are considered to be dielectrics (insulators). Therefore the electrical conductivity of a given segment of a saline and/or sodic soil may be considered a function of the

electrical conductivity of the pore solution (EC_w), the volumetric water content (θ), the tortuosity (T), and the specific surface conductivity (EC_s) of the soil. Specific surface conductivity, a parameter which is dependent on surface charge and exchangeable ions, may be appreciable in soils with high contents of fine size particles particularly if the cation exchange capacity of the mineral is high. In the case of saline and sodic soils, because of the greater abundance and mobility of soluble salts than the exchangeable cations, the contribution of specific surface conductvity to the bulk soil electrical conductivity has not been considered as significant. For a given temperature, Rhoades et al. (1976) argued that

$$EC_a = f\ (EC_w,\ \theta,\ T,\ EC_s) \qquad (1)$$

Since tortuosity and specific surface conductivity are properties of the soil's solid-phase while volumetric water content and electrical conductivity of the pore solution are properties of soil's liquid-phase; therefore for a given soil,

$$EC_a = f\ (EC_w,\ \theta)_T,\ EC_s \qquad (2)$$

If the bulk soil electrical conductivity measurement is made at a given water content,

$$EC_a = f\ (EC_w)_\theta,\ T,\ EC_s \qquad (3)$$

Subsequently, for any given soil, the electrical conductivity of a soil saturation extract (EC_e) is uniquely related to EC_w,

$$EC_a = f\ (EC_e)_\theta,\ T,\ EC_s \qquad (4)$$

Rhoades and Ingvalson (1971) presented eq. (3) in a more mathematical manner by assuming that EC_w and EC_s were resistors in parallel, or

$$EC_a = (EC_w\ \theta)\ (T) + EC_s \qquad (5)$$

where T, which they also referred to as "transmission coefficient", is empirically determined and related to θ as,

$$T = a\ + b \qquad (6)$$

where "a" and "b" are evaluated by linear regression analysis.

Rhoades and Halvorson (1977) demonstrated that if the EC_a measurements are made for a given soil type at a reference water content, EC_a could be expressed in terms of EC_e and EC_s according to eq. (4) which would take the form,

$$EC_a = A\ (EC_e) + EC_s \qquad (7)$$

where A is a constant evaluated graphically by plotting values of EC_a against EC_e.

Eq. (7) thus provides the theoretical basis of using soil resistivity as an alternate measure of diagnosing soil salinity. From eq. (5) it is obvious that EC_a is positively correlated with the soil volumetric water content (θ) and the electrical conductivity of soil solution (EC_w), provided all the other factors in the equation are constant. It is also clear that inherent pore and constituent characteristics are important contributors to bulk soil electrical conductivity as reflected in the transmission coefficient (T) and specific surface conductivity (EC_s), respectively. Sauer et al. (1955) suggested that the electrical conductivity of columns of ion exchange resin spheres saturated with solutions of electrolytes could be

represented by three resistances in parallel. Based on this model, Shainberg, Rhoades and Prather (1980) developed an equation to evaluate the dependence of bulk soil electrical conductivity over a wide range of soil solution concentrations with particular emphasis on soil solution concentrations below 4mmho/cm. The equation took the form of:

$$EC_a = \frac{(EC_s)(EC_w)}{(1-d)/d\ (EC_w) + (EC_w)} + \frac{EC_w}{F} \qquad (8)$$

where d is the thickness of the solid phase and F the formation factor with the convention that $1/F = \theta T$. At high soil solution concentration i.e. $EC_w > EC_s$ eq. (8) reduces to eq. (5). At low soil solution concentration, the first part in eq. (8) determines the intercept of the EC_a vs. EC_w curve.

Soils with high salt content (saline or saline/sodic soils) would have higher bulk soil electrical conductivity levels via the high EC_w; while those with montmorillonitic mineralogy and high clay content (< 2 m particles) are also expected to attain high EC_a through the characteristically high EC_s.

Application of the Bulk Soil Electrical Conductivity in Soil Salinity Measurements

Earth resistivity has long been employed by geophysicists to locate ground water (Meidav, 1960; McDonald and Wantland, 1960); however, its usefulness in the assessment of soil salinity was not realized until the early 1970's. Since then many experiments concerning bulk soil electrical conductivity at various soil depths on different soils have been performed by workers with the aid of the

Wenner Array arrangement or the EC-Probe (Rhoades and Ingvalson, 1971; Rhoades and Schilfaarde, 1976; Halvorson and Rhoades, 1976). Similar experiments were carried out also on field mapping of soil electrical conductivity to delineate surface and sub-surface boundaries of encroaching and developed saline seeps (Halvorson and Rhoades, 1976).

Rhoades and Ingvalson (1971) used an array of 4 electrodes in a Wenner Array arrangement to measure the average salinity of a large soil volume, about $5\pi a^3/6$, where "a" is the inter-electrode distance and the apparent bulk soil electrical conductivity was evaluated as:

$$EC_a = \frac{(17.133)(f_t)}{(a)(R_t)} \qquad (9)$$

where R_t is the measured resistance in ohms; "a" is the equidistance interelectrode spacing in meters and f_t is the factor to adjust the reading to the reference temperature of 25°C. They also confirmed that widening the distance between adjacent electrodes increased the extent of the volume measured.

Halvorson and Rhoades (1974), by using the Wenner Array arrangement, obtained plots of soil electrical conductivity (EC_a) vs. inner electrode spacing (a) at two different periods of the year near Sidney, Montana and used them to identify potential saline seep areas. Rhoades (1975) obtained soil resistance measurements to measure, map and monitor field salinity and water table depth.

Rhoades and Schilfaarde (1976) described a method of mounting the four electrodes on a probe (EC-probe) to determine soil salinity in small soil volumes where the field salinity was not laterally uniform. The EC-probe measures the average salinity of a soil volume, about $5\pi a^3/3$, where "a" is the spacing between the pairs of adjacent

electrodes. The bulk soil electrical conductivity is measured within soil intervals of 0 to 0.305, 0.305 to 0.610, 0.610 to 0.915 and 0.915 to 1.220 meters where the probe is centered at 0.153, 0.459, 0.765 and 1.071 meters in depths, respectively. The apparent bulk soil electrical conductivity EC_x (mmho/cm) within a soil interval is calculated as the following,

$$EC_x = (K)(f_t)/R_t \qquad (10)$$

where K is an empirically determined cell constant for the probe in 10^3/cm and f_t is the correction factor to adjust the resistance reading (R_t) to 25°C. Halvorson and Rhoades (1976) further demonstrated the usefulness of the 4-electrodes method to delineate dryland saline seeps in Northeastern Montana.

The effect of soil water content and soluble salt concentration on bulk soil electrical conductivity has been studied by several investigators. Rhoades and Ingvalson (1971) recommended that bulk soil electrical conductivity measurements be made 2 to 3 days after irrigation to allow sufficient drainage. Halvorson and Rhoades (1974) suggested that the 4-electrode method be applied to fallow land and cropped land in the spring and immediately after rainfall to allow enough drainage. Shea and Luthin (1961) traced salt movement in a soil profile by placing a 4-electrode unit at various depths in the soil. They discovered that error of up to 14% could be obtained in the salinity measurements without correction for water content. Gupta and Hank (1972) adjusted two soils to various water and salt (KCl) contents in special conductivity cups and determined the bulk soil electrical conductivity with a 4-probe (electrode) system. They

observed that the bulk soil electrical conductivity increased markedly as the water content and salt content increased. Kirkham and Taylor (1970) compared bulk soil electrical conductivity readings with gravimetric water content and obtained a correlation coefficient between them of 0.83, but with high variability. Edlefson and Anderson (1974) observed that a very small change in soil water content, near permanent wilting point ($\sim$ 15 bar tension), caused a large change in bulk soil electrical conductivity. Rhoades, Raats and Prather (1976) with the aid of a mini Wenner Array arrangement, demonstrated the dependence of bulk soil electrical conductivity on soil water content and electrical conductivity of soil solution by using undisturbed (lucite) core samples from four soil types in California. They also established threshold water contents (θ_t) for Pachappa fsl, Indio vfsl, Waukenal and Domino cl soils, which were 7.0, 9.0, 5.0 and 12.0%, respectively. More recently, Shainberg, Rhoades and Prather (1980) reported that the bulk soil electrical conductivity increased non-linearly with respect to the soil solution electrical conductivity in the low range of salt concentration range (< 2-3 mmho/cm); however in the high salt concentration range, a straight line relationship was obtained).

The Significance of Surface Conductance and Specific Surface Conductivity in Determining Bulk Soil Electrical Conductivity Values

The contribution of surface conductance and specific surface conductivity to the bulk soil electrical conductivity depends on the nature of the soil. The surface conductance measures the product of

the number of counter-ions per unit area of the surface and the average mobility of these ions on the surface of the colloidal system, if the colloidal particles themselves are ideal dielectrics. For conducting particles this term would encompass additional contributions depending on the dielectric constant of the colloid. Surface conductance has attracted the attention of many researchers and the systems studied varied from clay minerals (van Olphen, 1957) to biological cells (Maczuk and Pauly, 1962) and proteins (Oncley, 1942; Takashima and Schwan, 1965).

Maxwell (1891) was the pioneer to formulate the behavior of composite dielectrics which was later extended by Wagner (1913, 1914) to stress the importance of frequency of the electric field and the geometry of the system in the assessment of the surface conductance.

van Olphen (1957) reported the surface conductance of Na-bentonite to be between 3.2 and 5.8×10^{-9} mho. Cremers and Laudelout (1966) established surface conductance for Na-Bertean Montmorillonite (9.2%), Na-Wyomong Bentonite (5.7%), Na-Zettlite Kaolinite (29.1%) and Na-Boluvit Kaolinite (29.6%) to be 1.78, 1.41, 2.20 and 2.89×10^{-9} mho, respectively.

Later, Cremers and Laudelout (1966) demonstrated that the change of surface mobility of an ion is a function of clay content and they derived an equation relating the electrical conductivity of a "salt free" clay plug to surface conductance,

$$K_g = (K_s)(S_u)/(F)(\phi) \qquad (11)$$

where K_s represents surface conductance in mho; K_g is the electrical conductivity of the gel in mho/cm; F is the formation factor; ϕ is

the porosity of the gel and S_u is the exposure area in cm^2/cm^3 (area of solid per unit volume of gel).

Weiler and Chasusidon (1968) observed that the electrical conductivity of four clay gels measured at the frequency of 1000HZ was affected by the nature of exchangeable cations in the order of:

Na-montmorillonite > Li-montmorillonite > K-montmorillonite > Cs-montmorillonite

They derived a relationship between surface conductance and specific surface conductivity,

$$EC_S = (4)(K_S)/(\pi)(a) \qquad (12)$$

where EC_S is the specific surface conductivity of the mineral in mho/cm; K_S is the surface conductance of the similar mineral in mho; "a" is the effective radius of the dispersed phase in cm. The frequency dependence of the electrical conductivity of four clay gels was also observed by the authors, though the variation was rather small. In this study, the specific surface conductivity of various Ca and Na saturated minerals was evaluated by using eq. (12) at two frequencies, i.e. 80HZ and 1KHZ.

Shainberg and Levy (1975) with the aid of the iso-conductivity theory, calculated the surface conductance of Upton Wyoming Montmorillonite (2.5%) to be 3.33×10^{-9} mho. This method was also employed in determining the surface conductance of various Ca and Na saturated minerals in this study.

Rhoades, Raat and Prather (1976) obtained specific surface conductivity values of 0.18, 0.25, 0.40 and 0.45 mmho/cm for Pachappa fsl, Indio vfsl, Waukena l and Domino cl soils, respectively,

by extrapolating the graph of bulk soil electrical conductivity vs. electrical conductivity of liquid-phase (EC_a vs. EC_w) to y-axis. They demonstrated, as expected, specific surface conductivity was greater for finer-textured soils. Therefore the higher the clay content of the soil, the greater would be the bulk soil electrical conductivity, provided all the other factors are constant.

Shainberg, Rhoades and Prather (1980) observed the general positive relationship between soil ESP and specific surface conductivity was not conclusive because of the scattering in the data. They also demonstrated that specific surface conductivity increased with increasing clay content (< 2 μm particles) of the soil.

MATERIALS AND METHODS

Materials

Soils

Four Soil Orders were represented in this study and they were selected according to their mineralogical and water retention characteristics. They were:

1.) Aridisol (Kawaihae Series)

2.) Oxisol (Molokai Series)

3.) Vertisol (Lualualei Series)

4.) Inceptisol (Kukaiau Series)

The classification, mineralogical composition and chemical composition of each Series are listed in Tables 1, 2 and 3, respectively.

Standard clay minerals

The Ca and Na forms were prepared by equilibrating the following standard minerals with 1N $CaCl_2$ and 1N NaCl solutions for 2 weeks. The excess free electrolytes were eliminated by dialysis with semi-permeable visking bags in deionized water until they were freed of chloride as indicated by a negative $AgNO_3$ test. They were then dried by freeze drying and stored in plastic bottles. The four standard clay minerals were:

1.) Montmorillonite A (#26 Clay, Spur, Wyoming, 48W 1260, Wards Natural Sci. Establishment, Inc.)

2.) Montmorillonite B (Pea Sixe-Belle, Volelay, American Colloid Co.)

Table 1. Classificaton*/ of the selected soils

Series	Family	Greatgroup and subgroup	Depth (cm)
Kawaihae	Medial, ashy, iso-hyperthermic	Ustollic Camborthids	0-15
Molokai	Clayey, kaolinitic, isohyperthermic	Typic Torrox	0-15
Lualualei	Very fine, montmoril-lonitic, isohyperthermic	Typic Chromustert	0-15
Kukaiau	Thixotropic, isothermic	Hydric Dystrandepts	0-15

*/The classifcation information was obtained from Soil Survey of the State of Hawaii, Soil Conservation Service, United States Department of Agriculture.

Table 2. Mineralogical composition of the selected soils

Soil	A	F	G	G_o	He	Ha	I	K	Magh	Magn	Mi	C	C	Q	S
Kawaihae[a/]	2	3	-	4	4	-	-	5*	4	-	-	-	-	4	4
Molokai[a/]	3	-	3	4	3	5	-	3	3	5	-	-	-	4	-
Lualualei[b/]	-	-	-	-	4	-	-	4	-	-	-	-	4	5	1
Kukaiau[b/]	x+	-	4	4	-	-	-	-	3	-	5	-	-	4	-

[a/] Data obtained from Sinanuwong, Somsri. 1972. Cation Exchange Equilibria in Irrigated Tropical Soils. Ph.D. Dissertaiton, U. of Hawaii.

[b/] Data from Dangler, E. W. (unpublished data for the University of Hawaii, Institute of Tropical Agriculture Erosion Project).

* Unidentified member of the kaolinite group.

x+ Present in large amount but unable to quantify accurately.

Legend

A = Amorphous (including organic matter)
F = Feldspar
G = Gibbsite
G_o = Goethite
He = Hematite
Ha = Halloysite
I = Interstratified
K = Kaolinite
Mgh = Maghemite
Mgn = Magnetite
O = Olivine
Q = Quartz
S = Smectite
C = Calcite
Mi = Mica
1 = 40%
2 = 25-40%
3 = 10-25%
4 = 1-10%
5 = trace
- = not present

Table 3. Chemical characteristics of the selected soils

Series	Extractable cations[a/]				% OM[b/]	pH[c/]	EC[d/]
	Ca	Mg	K	Na			
	- - - -(meq/100g)- - - - -						(mmho/cm)
Kawaihae	4.65	5.03	0.31	3.48	0.67	6.84	0.36
Molokai	4.10	1.75	0.24	0.63	0.75	5.82	0.46
Lualualei	27.80	12.23	0.54	3.68	3.41	7.52	2.39
Kukaiau	2.68	0.16	0.13	1.08	17.84	5.45	0.34

[a/] By 1N ammonium acetate (adjusted to pH 7.0) method.

[b/] Organic matter content was obtained by the Walkley-Black method.

[c/] pH of the saturated soil paste.

[d] Electrical conductivity of the saturated soil extract at 25°C.

3.) Kaolinite (#7, Dixie Rubber Pit, Bath, South Carolina, Wards Natural Sci. Establishment, Inc.)

4.) Halloysite (#29, Wagon Wheel Gap, Colorado, Wards Natural Sci. Establishment, Inc.)

Synthetic minerals

1.) Iron hydrous oxide, fine (goethite)

2.) Iron hydrous oxide, coarse (goethite)

3.) α-iron oxide (hematite)

4.) Aluminum hydroxide (gibbsite/bayerite)

Methods

Soil sampling

The site of the sampled Kawaihae Series was about 2 miles from Kawaihae harbor along Highway 27 towards Hawi on the Island of Hawaii. The Molokai Series was sampled from a field of Oahu Sugar Company by Kunia Road, about 1/2 mile from the HSPA Experiment Station at Kunia on the Island of Oahu. The location of the sampled Lualualei Series was at the Lualualei Naval Air Radio Station at Lualualei on the Island of Oahu. The Kukaiau Series was collected from a field of Honokaa Sugar Company which was about 2 miles from Honokaa along Highway 24 towards Waipio on the Island of Hawaii.

The collected soils were sieved through a 20 mesh sieve, stones and gravels discarded, well mixed and stored in double plastic bags at the temperature of 5°C to preserve as much of the original properties as possible.

Mineral synthesis

The sesquioxides were synthesized by the methods described by El-Swaify and Emerson (1975) for iron hydrous oxide (fine and coarse) and Gastuche (1964) for aluminum hydroxide.

1.) Iron hydrous oxide (goethite)

Iron hydrous oxide was synthesized by titrating a 1N $FeCl_3$ solution with 1N NaOH solution very slowly to pH 6.0 and pH 12.0 for fine and coarse precipitates, respectively. The Ca and Na forms were prepared by equilibrating each of these sesquioxides with 1N $CaCl_2$ and 1N NaCl solutions for 2 weeks, respectively. The excess electrolytes in the sesquioxides were eliminated by dialysis with semi-permeable visking bags in deionized water until they were freed of chloride. They were then freeze-dried and stored in plastic bottles.

2.) α-Iron oxide (hematite)

The Ca and Na forms of iron oxide were prepared by firing a portion of each of the above freeze-dried Ca and Na forms iron hydrous oxide (coarse) in a furnace at 550°C for 4 hours.

3.) Aluminum hydroxide (gibbsite/bayerite)

Aluminum hydroxide was synthesized by titrating 0.1N $AlCl_3$ solution with 0.1N NaOH solution very slowly to pH 4.5. The Ca and Na forms were prepared by equilibrating the synthesized aluminum hydroxide with 1N $CaCl_2$ and 1N NaCl solution for 2 weeks, respectively. The excess electrolytes in the above two forms were eliminated by dialysis with semi-permeable visking bags in deionized water until they were freed of chloride. They were then freeze-dried and stored in plastic bottles.

Sample characterization

1. pH

The pH of saturated soil pastes, mineral suspensions and supernatants was determined by a Beckman Expandomatic pH meter equipped with reference and glass electrodes. The data are presented in Tables 3 and 5, respectively.

2. Exchangeable cations

The cations on selected soils (Ca, Mg, K and Na) were extracted with 1N CH_3COONH_4 solution adjusted to pH 7.0 and determined on an atomic absorption spectrophotometer. The data are shown in Table 3.

3. Cation exchange capacity (CEC)

Two methods were used:

i. Subsamples of the selected soils, Ca and Na forms of standard clay minerals and synthetic sesquioxides were leached with 1N CH_3COONH_4 solution adjusted to pH 7.0 and followed by displacement with 1N KCl solution and distillation of ammonia.

ii. Subsamples of the Ca and Na forms of dialyzed soils, standard clay minerals and sesquioxides were leached with 1N $Mg(NO_3)_2$ solution (pH 6.3). The leachates were collected and made up to volume. The amount of Ca and Na in the leachates were then determined by the atomic absorption spectrophotometer. The results of i and ii are presented in Tables 4 and 5.

Table 4. Exchange characteristics of the selected soils

Soil	Cation exchange capacity*/	
	"tradit"	"effect"
	- - - (meq/100g) - - -	
Na-Kawaihae	37.60**/	7.94
Ca-Kawaihae		14.13
Na-Molokai	19.43	9.22
Ca-Molokai		17.30
Na-Lualualei	46.65	80.47
Ca-Lualualei		91.49
Na-Kukaiau	63.10	2.83
Ca-Kukaiau		4.91

*/"Traditional" and "effective" cation exchange capacity as explained in item 3 (i) and 3 (ii) under Sample characterization, respectively.

**/The "traditional" cation exchange capacity of the untreated soils, i.e., not saturated by Na and Ca.

Table 5. Exchange characteristics, pH of suspensions and supernatants and zero point of charge of various minerals

Mineral	Cation exch. cap.[a]		Anion exch. cap.[b]	ZPC[c]	pH[d]	
	"tradit"	"effect"			susp.	sup.
	- -(meq/100g)- -		(meq/100g)			
Na-montmorillonite A	71.65	73.76	0.10	-[e]	5.40	5.54
Ca-montmorillonite A	62.32	74.13	0.31		8.70	7.20
Na-montmorillonite B	66.56	75.44	0.51	-[e]	8.02	7.92
Ca-montmorillonite B	65.08	82.92	0.00		8.85	7.90
Na-kaolinite	5.55	3.43	0.15	3.3-5.0[f]	6.76	6.45
Ca-kaolinte	3.33	2.79	0.19		5.30	5.60
Na-halloysite	5.19	2.78	0.26	3.3-5.0[f]	6.70	6.55
Ca-halloysite	5.00	3.53	0.26		6.53	6.70
Na-goethite (fine)	14.53	1.24	9.44	6.70[g]	4.94	5.15
Ca-goethite (fine)	10.36	0.46	11.85		4.48	4.63
Na-goethite (coarse)	1.20	1.31	0.45	6.70[g]	6.46	6.68
Ca-goethite (coarse)	0.83	1.28	0.00		8.47	7.35
Na-bayerite	0.74	1.01	1.39	7.50[h]	4.76	5.01
Ca-bayerite	0.16	0.38	1.23		4.80	4.90
Na-hematite	1.87	1.52	0.15	6.70[g]	7.95	7.69
Ca-hematite	1.68	2.42	0.00		9.50	9.20

[a] "Traditional" and "effective" cation exchange capacity as explained in 3 (i) and 3 (ii) under Sample characterization, respectively.

[b] Anion exchange capacity.

[c] Zero point of charge.

[d] pH of the 2.5% minerals' suspensions and supernatants.

[e] From Greenland, D. J., 1974.

[f] From Parks, G. A., 1967.

[g] From Parks, G. A., 1965.

[h] From Parks, G. A., 1965.

For convenience, the cation exchange capacity obtained by 1N $Mg(NO_3)_2$ and 1N CH_3COONH_4 methods is referred to as "effective" and "traditional" cation exchange capacity, respectively.

Except in the Lualualei Series, the "effective" cation exchange capacity is smaller than the "traditional" cation exchange capacity in each soil. The abnormal behavior exhibited by the Lualualei Seires might be due to the incompleted dialysis and/or contamination. Sinanuwong (1972) obtained a much smaller "effective" cation exchange capacity for the Lualualei Series at a comparable location.

The Na form of minerals possesses higher "traditional" cation exchange capacity values than those of the Ca counterparts. This may be attributed to the stronger specific adsorption of Ca against displacement or the dispersing effect of Na ions on the minerals thus exposing more exchangeable sites available for replacement by NH_4^+ ions. The "effective" cation exchange capacity is also larger than the "traditional" cation exchange capacity in Ca and Na montmorillonite (A and B), aluminum hydroxide, goethite (coarse) and Ca-iron oxide. This phenomenon may be attributed to the variation in the replacing power of NH_4^+, K^+ and Mg^{++} and/or the NH_4^+ ions fixation process. Gedroiz (1922) observed that the relative replacing power of certain ions depended on what cations were being replaced and its concentration. In the fine goethite, the "traditional" cation exchange capacity is much greater than the corresponding "effective" cation exchange capacity. El-Swaify and Sayegh (1974) attributed the overestimation of the magnitude of negative charges by the ammonium acetate method to the selective adsorption of CH_3COO^- ions at the soil surface thus

shifting the isoelectric points of the soils to lower values. In other oxidic systems, such as coarse goethite, hematite and bayerite, the phenomenon is not obvious.

Schachtsch (1940) discovered that the replacement of adsorbed ions by other ions was mineral dependent. Kelly (1964) summarized in a review paper that the replacing power of several cations was in the following order:

$$Ca^{++} > Mg^{++} > K^{+} > NH_4^{+} > Na^{+}$$

Tamimi (1964) reported the NH_4^+ fixing capacity for Lualualei (predominated by montmorillonitic materials) and Hilo series (mostly amorphous materials and gibbsite) to be 3.12 and 3.74 meq/100g, respectively. The occurrence of the NH_4^+ fixation process by soil constituents such as montmorillonite, allophane and aluminum hydroxide decreases the amount of adsorbed NH_4^+ to be replaced by K^+ (from 1N-KCl solution), thus lowering the "traditional" cation exchange capacity. The "effective" cation exchange capacity is highly correlated with the "traditional" cation exchange capacity ($r = 0.9498$). The "effective" cation exchange capacity is used to evaluate the "ideal" surface conductance of various minerals in this study.

4. Anion exchange capacity (AEC)

The anion exchange capacity of Ca and Na forms of standard clay minerals and synthetic sesquioxides were determined by the potentiometric titration of chloride in the 1N-$Mg(NO_3)_2$ leachates of the minerals by standardized $AgNO_3$ solution in the presence of a chloride sensitive electrode. The data are shown in Table 5. All of the minerals, except iron hydrous oxide (fine) and aluminum hydroxide,

do not have significant "effective" anion exchange capacity. Two factors may have contributed to this situation: i) The NO_3^- ions are unable to replace most of the Cl^- ions on the anion exchange sites thus making the real anion exchange capacity. ii) Also shown on the same table is the pH of the suspensions and supernatants in which these minerals are equilibrated. It is obvious that the suspensions and supernatants of high pH values are always associated with the low "effective" anion exchange capacity. For example, iron hydrous oxide (fine), which has the highest "effective" anion exchange capacity established in this study, is associated with the lowest suspension and supernatant pH. A high pH system is dominated by a high concentration of OH^- ions, thus forming a net negative charge in variable change systems and an unfavorable environment for the adsorption of anions. The principle of zero point of charge (ZPC) offers a quantitative explanation for the above behavior. The approximate ZPC of various standard clay minerals and synthetic sesquioxides is shown in Table 8. The relatively high "effective" anion exchange capacity possessed by iron hydrous oxide (fine) and aluminum hydroxide is not surprising since their suspensions and supernatants are at pH values that are much lower than their respective ZPC values. Montmorillonite is not amphoteric and contains few or no pH dependent charges. This explains the very low "effective" anion exchange capacity values determined for both sources of this mineral. The suspensions or supernatant pH of kaolinite, halloysite, goethite (coarse) and iron oxide are well above their corresponding ZPC's which explains the low AEC's.

5. Electrical conductivity of soil saturation extract (EC_e)

The EC_e was determined by a Beckman Conductivity Bridge (RC-16C) and the result for untreated soils are shown in Table 3.

6. X-ray diffraction analysis

The mineralogical identification of various synthetic sesquioxides was carried out by a Philip Norelco X-ray diffractometer with Cu K_α radiation and graphite monochrometer.

The X-ray diffractograms of the synthetic iron hydrous oxides (fine and coarse), iron oxide and aluminum hydroxide are shown in Appendix A. As intended, the iron hydrous oxide which was precipitated at pH 6.00 appeared to be mostly fine graded and amorphous. The iron hydrous oxide which was precipitated at pH 12.00 was diagnosed as coarse crystals of α -FeOOH (goethite). The iron oxide, prepared by firing the coarse hydrous oxide for 4 hours at 550°C, showed α -Fe_2O_3 (hematite) peaks. The synthetic aluminum hydroxide was identified to be bayerite (γ -$Al_2O_3 \cdot 3H_2O$).

7. Particle density

The particle density of various soils and minerals was determined by the pycnometer method (Blake, 1965). The results are presented in Tables 6 and 7, respectively.

8. Effective radius

Assuming the dispersed phase to be spherical in shape, the effective radius of various minerals (similar to that employed in Stoke's sedimentation) was evaluated with the aid of the specific surface area and the particle density determined previously. The formula takes the form of:

$$a = 3/(P_p)(S) \qquad (13)$$

Table 6. Particle density, bulk density and porosity of the selected soils

Series	Particle density (g/ml)	Bulk density (g/ml)	Porosity (%)
Kawaihae	2.46	1.14	53.66
Molokai	2.32	1.04	55.17
Lualualei	2.45	1.05	57.14
Kukaiau	2.41	0.50	79.25

Table 7. The particle density and effective radius of various minerals

Mineral	Particle density (P_p) (g/cm^3)	Average effective radius(a) ($m \times 10^{-9}$)
Na-montmorillonite A	1.89	5.14
Ca-montmorillonite A	2.23	2.99
Na-montmorillonite B	1.77	5.31
Ca-montmorillonite B	2.13	3.06
Na-kaolinite	2.35	27.2
Ca-kaolinite	2.44	34.2
Na-halloysite	2.32	40.4
Ca-halloysite	2.32	43.1
Na-goethite (fine)	3.20	2.62
Ca-goethite (fine)	2.87	2.84
Na-goethite (coarse)	3.16	8.74
Ca-goethite (coarse)	3.48	6.38
Na-bayerite	2.18	47.5
Ca-bayerite	2.37	158.0
Na-hematite	4.11	28.1
Ca-hematite	5.23	12.0

where "a" is the effective radius in cm; P_p the particle density in gm/cm^3 and S the specific surface area in cm^2/gm. The result is shown in Table 7.

9. Bulk density

The bulk density of various untreated soils was determined by the core method (Blake, 1965). In the study of the effect of packing on bulk soil electrical conductivity, bulk density was adjusted during soil packing to desired values. The results are shown in Table 6.

10. Particle size distribution

The particle size distribution of the selected soils and standard clay minerals was determined by shaking 20g of each of these materials in a Spex Mixer Mill with a soil:solution ratio of 1:3 for 20 minutes (Lim, 1976). The dispersing solution was prepared by mixing 8 ml of 10% sodium hexametaphosphate solution with 4 ml of 1N NaOH solution and the resulting solution was made up to 60 ml with deionized water. The suspension was then suspended in a liter-cylinder with deionized water. Silt and clay fractions were determined by the Plummet Balance (Marshall, 1965). Sand size particles were determined by differences and also by sieving and weighing. The results are shown in Tables 8 and 9.

11. Specific surface area (S)

Three approaches were used to determine the specific surface area of various Ca and Na standard clay minerals and synthetic sesquioxides:

i. N_2 gas adsorption

A Perkin-Elmer Shell model 212D Sorptometer was used. This involves a stream of gas, consisting of N_2 as an

Table 8. Particle size distribution of the selected soils

Series	Sand*/	Silt**/	Clay#/
		(%)	
Kawaihae	4.98	40.93	54.10
Molokai	5.28	34.17	60.55
Lualualei	4.40	31.90	63.70
Kukaiau	26.33	35.33	38.35

*/ > 50 µm

**/ 2-50 µm

#/ < 2 µm

Table 9. Particle size distribution of the selected standard clay minerals

Mineral	Sand*/	Silt**/	Clay#/
	- - - - - - - (%) - - - - - - - - -		
Montmorillonite A	2.30	30.10	67.60
Montmorillonite B	0.00	24.32	75.68
Kaolinite	2.94	8.62	88.44
Halloysite	5.97	11.43	82.60

*/ > 50 μm

**/ 2-50 μm

#/ < 2 μm

adsorbate and helium as an inert carrier. The specific surface area of the mineral of interest was determined by measuring the amount of N_2 adsorbed between a range of P/P_o = 0.21 and P/P_o = 0.33. Prior to all measurements, samples were degassed overnight in a sand bath at a temperature of 110°C with a constant stream of helium gas passing through them in order to drive off any interfering moisture or residual gases. The BET equation was employed to calculate the specific surface area of the mineral of interest.

ii. H_2O vapor adsorption

The Ca and Na forms of various standard clay minerals and synthetic sesquioxides were brought into equilibrium with constant relative humidities in five different desiccators containing saturated solutions of NaCl, $Ca(NO_3)_2 \cdot 4H_2O$, $MgCl_2 \cdot 6H_2O$, CH_3COOK and LiCl. The relative humidities (P/P_o) of atmospheres in equilibrium with these saturated solutions were 75%, 50%, 33%, 20% and 11%, respectively. Four weeks were required for equilibrium. The minerals were weighed, oven-dried, moisture content calculated and the specific surface area of each was calculated by the BET equation.

iii. H_2O vapor desorption

The Ca and Na saturated montmorillonite A and B only were made into slurries with deionized water. The slurries were brought into equilibrium with constant humidities as

in the H_2O vapor adsorption method. After 4 weeks of equilibration, the specific surface area of the mineral of interest was determined in the same manner as ii. The results of i, ii, and iii are presented in Table 10.

The extremely small specific surface areas of montmorillonite A and B obtained from the low temperature N_2 adsorption revealed that these substances possess internal surface which are not accessible to N_2 molecules as suggested by Makower and Alexander (1938). Quirk (1955) assembled data from papers authored by Alexander and Haring (1936); Byers, Alexander and Holmes (1935); Goates and Hatch (1953); Keenan, Mooney and Wood (1952); and Makower, Shaw and Alexander (1938) and concluded that values of specific surface area determined by H_2O vapor adsorption were greater than those obtained from N_2 adsorption; however, aside from montmorillonite, no such trend was conclusively observed in this study. Since the N_2 adsorption method does not measure the internal area, the specific surface area determined by this method for montmorillonite A and B is excluded from use. Interestingly, the specific surface areas determined for other minerals is highly correlated with those found by H_2O vapor adsorption method ($r = 0.9917$).

The specific surface areas determined by the H_2O vapor desorption technique were slightly smaller than those

Table 10. Specific surface areas of various minerals determined by low temperature N_2 adsorption, H_2O vapor adsorption and vapor desorption

Mineral	Specific surface area		
	N_2 adsorption	H_2O adsorption	H_2O desorption
	(m^2/g)		
Na-montmorillonite A	6	307	327
Ca-montmorillonite A	27	450	458
Na-montmorillonite B	2	319	332
Ca-montmorillonite B	35	461	502
Na-kaolinite	52	47	
Ca-kaolinite	29	36	
Na-halloysite	38	32	
Ca-halloysite	21	30	
Na-goethite (fine)	360	357	
Ca-goethite (fine)	323	368	
Na-goethite (coarse)	139	109	
Ca-goethite (coarse)	120	135	
Na-bayerite	24	29	
Ca-bayerite	9	8	
Na-hematite	29	26	
Ca-hematite	49	48	

obtained by the H_2O vapor adsorption method. This might be due to the effect of hysteresis in the adsorption and desorption cycle as expected for porous system and as previously demonstrated by Mooney, Keenan and Wood (1952). For the reason of consistency, surface areas determined by the H_2O vapor adsorption technique were used to evaluate the surface conductance of various minerals.

12. Bulk soil electrical conductivity (EC_a) .

Lucite cores measuring 8.8 cm in diameter and 5.3 cm in height were packed with soil to desired packing density. The soil was then equilibrated with solutions of desired concentrations. Eight electrodes were inserted at 45° intervals into side openings on the core. Any four adjacent electrodes were regarded, at a given measurement, as Wenner Array arrangement--the outer two were current electrodes and the inner two potential electrodes. By rotating the conections during resistivity measurements, eight independent values on any core soil sample were obtained and the mean was recorded. The cell constant of each core was determined by placing 0.01N KCl solution (with an electrical conductivity of 0.41 mmho/cm at 25°C) into the core and the mean of eight independent electrical conductivity readings was recorded and adjusted to 25°C. The cell constant of the core was then calculated by dividing the known electrical conductivity of 0.01N KCl by the adjusted value. Hanging water columns (below 100 cm suction) and extraction in a pressure plate apparatus were employed to adjust the water content of the core samples. The water content of the core sample (by weight) was determined by weighing the tared core after

each equilibration and was finally converted into volumetric basis by multiplying the soil bulk density. The bulk soil electrical conductivity was made by a Martek Meter to which the four adjacent electrodes (Wenner Array) were attached.

13. Surface conductance (K_s)

Two approaches were used to evaluate the surface conductance of various Ca- and Na-saturated minerals. The first approach was based on the assumption that all Ca or Na ions are distributed on an equipotential surface and their mobilities are identical as those in dilute aqueous solutions. The "ideal" surface conductance was then calculated by multiplying the ionic equivalent conductivity with the surface charge density as outlined by Shainberg and Levy (1975):

$$K_s = L \times d \qquad (14)$$

where K_s is the surface conductance in mho; L the ionic equivalent conductivity in mho cm^2 eq^{-1} at 25°C (equal to 50.11[1/] mho cm^2 eq^{-1} and 50.95[1/] mho cm^2 eq^{-1} for Na and Ca ions, respectively) and d is the charge density at the clay surface in eq cm^{-2}.

The second approach is based on the concept of iso-conductivity point (Dakshinamurti, 1960; Cremers and Landelout, 1965) and formation factor, F (Cremers and Laudelout, 1965; Waxman and Smith, 1968). A series of nine 2.5% suspensions of each Ca- and Na-saturated standard clay minerals and synthetic sesquioxides was prepared in $CaCl_2$ and NaCl solutions, respectively. The solutions' concentration were 0.00, 0.0001, 0.001, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.10 N.

[1/] Data obtained from "Fundamentals of Physical Chemistry." Samuel H. Maron and Jerome B. Lando. p. 510.

After a 24 hour equilibration period (at 25°C), the electrical conductivity of each suspension was measured. The suspension was then centrifuged and the electrical conductivity of the supernatant was determined. The formation factor, F, was obtained by taking the slope of the graph of electrical conductivity of supernatant vs. electrical conductivity of suspension (Y vs. X). The iso-conductivity, which was defined as the conductivity point at which both effects balanced each other, namely when the suspension's electrical conductivity was equal that of the supernatant, was determined graphically. The surface conductance of the mineral of interest, was evaluated by the equation derived by Cremers and Landelout (1965):

$$K_s = (K_{iso})(K)/(P_p)(S) \qquad (15)$$

where K_{iso} is the iso-conductivity point in mmho/cm; S the specific surface area of the mineral in cm^2/g, P_p the particle density of the mineral in gm/cm ; K_s the surface conductance of the mineral in mmho and K is a parameter which depends on the axial ratio of the particles. K is related to the porosity of the mineral in the following manner:

$$F = 1 + K\ (1-\phi/\phi) \qquad (16)$$

where F is the formation factor and ϕ is the porosity of the mineral gel of interest. For convenience K was referred to as the geometry factor in this study.

The electrical conductivity of both suspensions and supernatants were measured at two frequencies (85 HZ and 1 KHZ) with a Beckman Conductivity Bridge (RC-16C). A sample calculation of the surface conductance of Na-kaolinite is shown in Appendix F.

14. Specific surface conductivity (EC_s)

The specific surface conductivity of each Ca- and Na-saturated mineral was determined by the formula derived by Weiler and Chaussidon (1965):

$$EC_s = (4)(K_s)/(\pi)(a) \qquad (17)$$

where K_s is the surface conductance in mmho; "a" the effective radius of the dispersed phase in cm and EC_s the specific surface conductivity in mmho/cm. A sample calculation of the specific surface conductivity is presented in Appendix F.

Experimental Variables

Effects of liquid-phase electrical conductivity (EC_w), soil exchangeable sodium percentage (ESP) and volumetric water content (θ) on bulk soil electrical conductivity (EC_a)

There were four levels of liquid-phase electrical conductivity (EC_w), six levels of soil exchangeable sodium percentage (ESP) and seven levels of volumetric water content (θ) on four soils with three replicates of each. The four levels of EC_w were 4, 8, 12 and 20 mmho/cm, while the six rates of soil ESP corresponded to SAR[2/] values of 0, 10, 20, 40, 100 and ∞, respectively. $CaCl_2$ and NaCl were

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2/ The U.S. Salinity Laboratory equation (1954) which related the soil ESP to the SAR of the equilibrating solution is:

$$ESP = \frac{100(-0.0126 + 0.01475SAR)}{1+(-0.0126 + 0.01475SAR)}$$

where ESP is the soil exchangeable sodium percentage and SAR the sodium adsorption ratio of the equilibrating solution expressed in the following manner:

$$SAR = (Na^{1+}) \,/\, \sqrt{1/2\ (Ca^{2+} + Mg^{2+})}$$

in which ionic concentrations are expressed as meq/l.
However Sinanuwong (1972), working on tropical soils, related these two parameters in a different way:

$$ESP = \frac{100(0.021 + 0.011SAR)}{1+(0.021 + 0.011SAR)}$$

According to these equations the corresponding ESP values to the above SAR levels are 0, 11.89, 22.02, 36.60, 59.39 and 100% (USSL) or 0, 11.58, 19.42, 31.55, 52.85 and 100% (Sinanuwong), respectively. The quantity of $CaCl_2$ and NaCl required to prepare solutions of desired SAR and EC_w is shown in Appendix B (based on the U.S. Salinity Laboratory equation).

used to establish the desired solution EC_w and SAR. About 10 pore volumes were used to leach the soil in the core with the desired solution. The seven levels of θ were established by draining the saturated columns under 0, 0.05, 0.1, 0.3, 2.0, 4.0 and 8.0 bars of tension.

Effects of packing and water content on bulk soil electrical conductivity

Three levels of packing density were studied on the four soils. These were 1.0, 1.1 and 1.2 times that of the range actually encountered in natural core of each soil. For this part of the study, the EC_w was 12 mmho/cm and the SAR was 10. The EC_a measurements were made at 0, 0.05, 0.1 and 2 bars of tension, respectively.

The effect of mineralogy on surface conductance and specific surface conductivity

The surface conductance (K_s) and specific surface conductivity (EC_s) of the Ca-and Na-saturated standard clay minerals and synthetic sesquioxides described in the early part of this section were determined.

RESULTS AND DISCUSSION

The Dependence of Bulk Soil Electrical Conductivity (EC_a) on Liquid-phase Electrical Conductivity (EC_w), Soil Volumetric Water Content (θ), Soil Exchangeable Sodium Percentage (ESP) and Packing Density

Effects of liquid-phase electrical conductivity (EC_w) and soil volumetric water content (θ)

Rhoades et al. (1976) showed the dependence of bulk soil electrical conductivity on electrical conductivity of the soil solution, soil volumetric water content, soil pore geometry and specific surface conductivity. Their relationship is represented by eq. (5) in the literature review section. When the transmission coefficient or pore geometry (T) term in eq. (5) is substituted by $a\theta + b$ as given by eq. (6) in the same section, eq. (5) becomes

$$EC_a = (EC_w)(\theta)(a\theta + b) + EC_s \qquad (18)$$

When the soil is subjected to drying as in the field condition, $(EC_w)(\theta)$ tend to remain relatively constant since any loss of water through evapo-transpiration is directly compensated by a proportional increase of soil solution concentration. However in this laboratory study, the predominance of drainage instead of drying does not allow a balancing effect between these two parameters. Thus the effect of change in soil water content on bulk soil electrical conductivity is expected to be higher than in the field condition, and indeed somewhat experimental in nature. After collecting terms, eq. (18) becomes

$$EC_a = (EC_w)(a)(\theta)^2 + (EC_w)(\theta)(b) + EC_s \qquad (19)$$

Eq. (19) is a polynomial predicting that at each soil solution concentration, bulk soil electrical conductivity is positively related to the soil volumetric water content in a non-linear manner.

Plots of EC_a against θ at different EC_w and ESP for the four soils are shown in Figs. 1, 2, 3 and 4. As predicted by eq. (19), EC_a increases non-linearly at each EC_w with increasing θ. The effect of EC_w on EC_a is more prominent at high θ than at low θ as indicated by the converging of the curves to a rather small area at low θ. At a water content of as low as 25%, Lualualei Series still possesses significant bulk soil electrical conductivity values at all soil solution concentrations investigated in this study. Kukaiau Series, which provides the other extreme, shows no significant bulk soil electrical conductivity below a water content of 35%; Molokai and Kawaihae Series exhibit an intermedian behavior. The response of bulk soil electrical conductivity to soil solution concentration and soil volumetric water content is not identical among the four soils. In general the magnitude of the bulk soil electrical conductivity under identical conditions is in the following order:

Lualualei > Molokai $\sim$ Kawaihae > Kukaiau

Eq. (5) predicts that at a given θ, EC_a is positively related to EC_w in a linear fashion. The values of EC_a and EC_w for a given θ at each ESP level were obtained from the EC_a vs. θ curves shown above by drawing vertical lines at given θ values (on x-axis) and obtaining respective EC_a values at the intersection points. An example of this relationship for each soil at the ESP = 22.0 is shown in Fig. 5. The specific surface conductivity (EC_s), according to eq. (5), is the

Fig. 1. Plots of bulk soil electrical conductivity, EC_a, vs. soil volumetric water content, θ, for Kawaihae Series at different exchangeable sodium percentage (ESP).

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

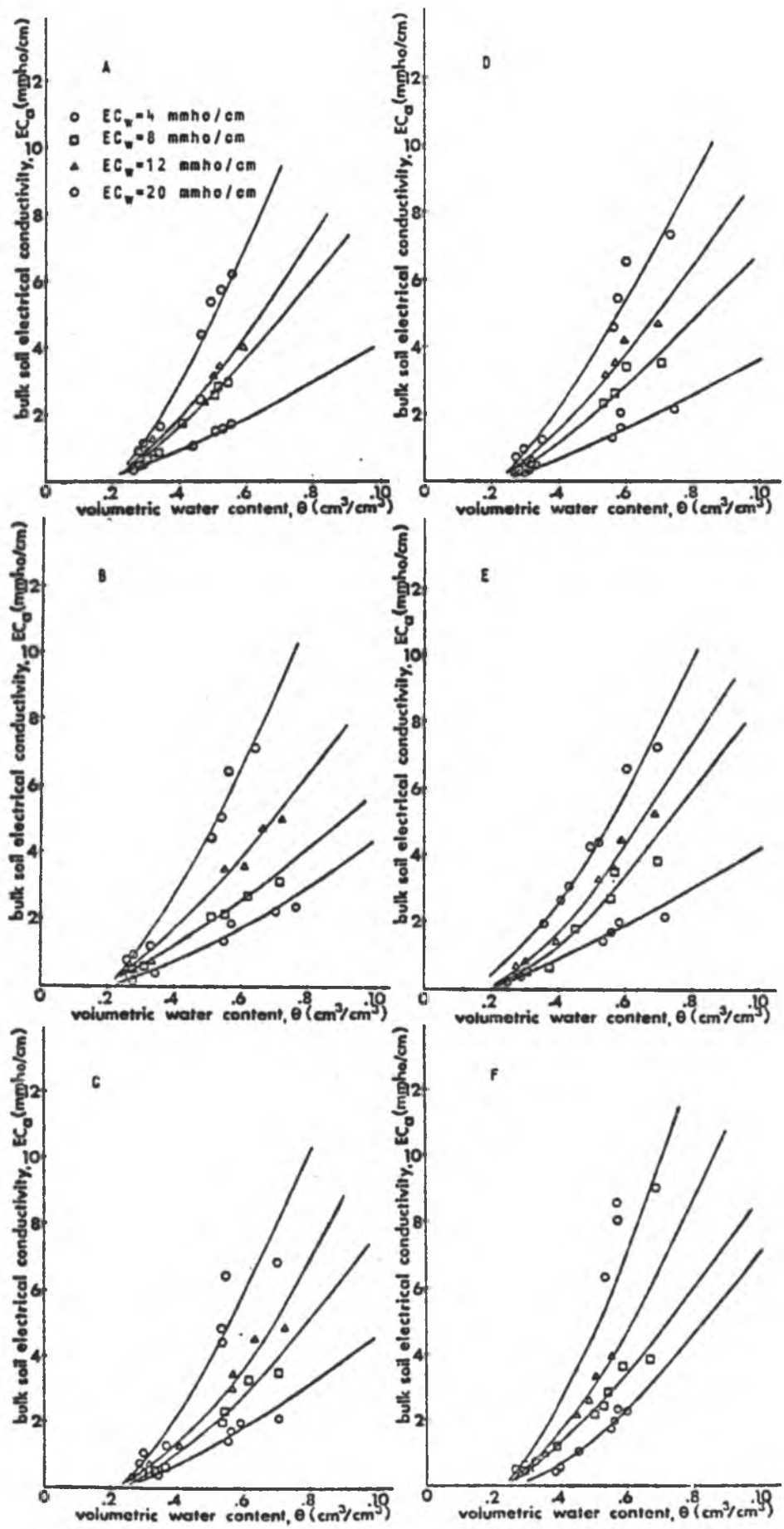


Fig. 2. Plots of bulk soil electrical conductivity, EC_a, vs. soil volumetric water content, θ, for Molokai Series at different exchangeable sodium percentage (ESP).

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

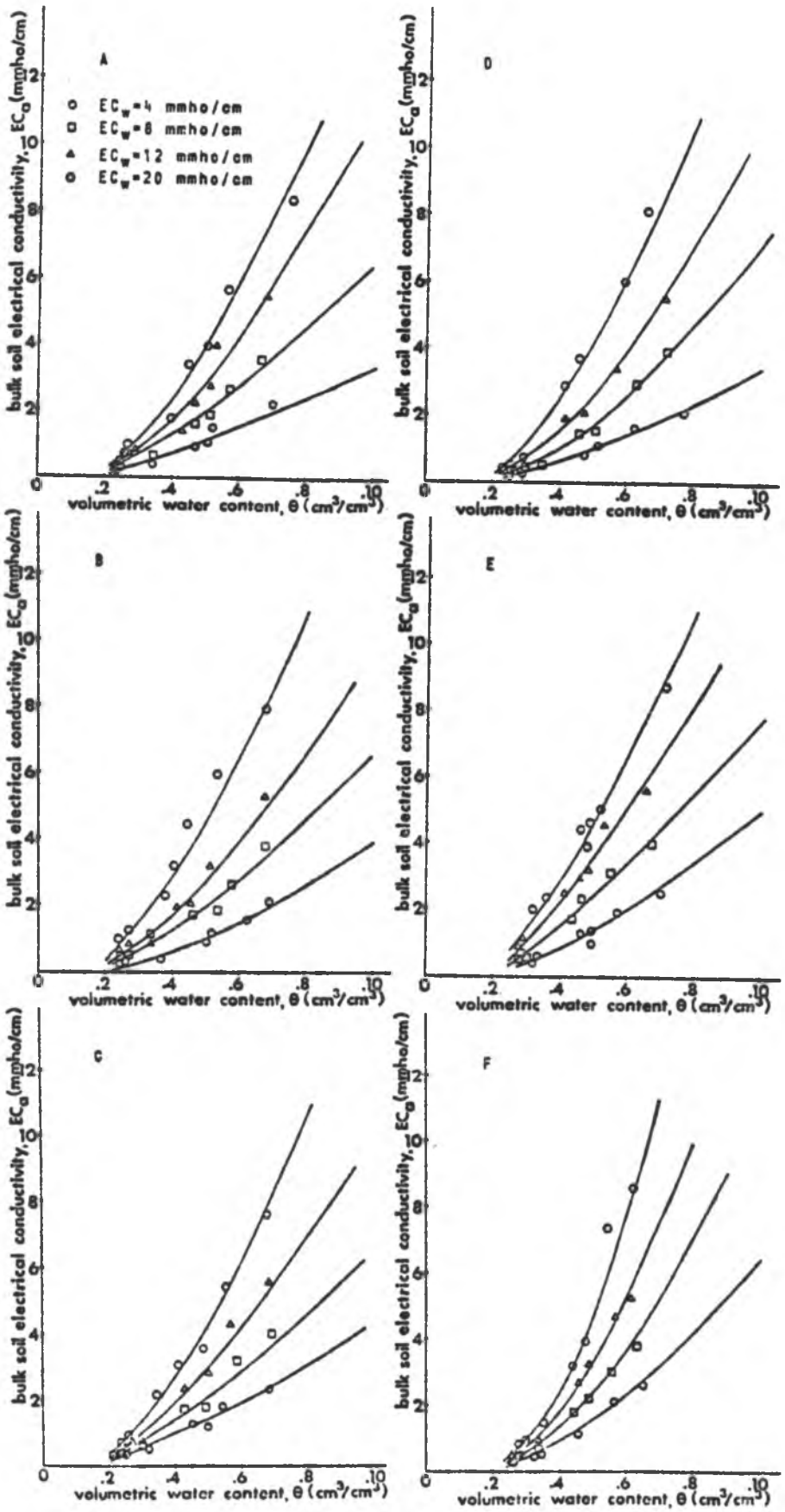


Fig. 3. Plots of bulk soil electrical conductivity, EC_a, vs. soil volumetric water content, θ, for Lualualei Series at different exchangeable sodium percentage (ESP).

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

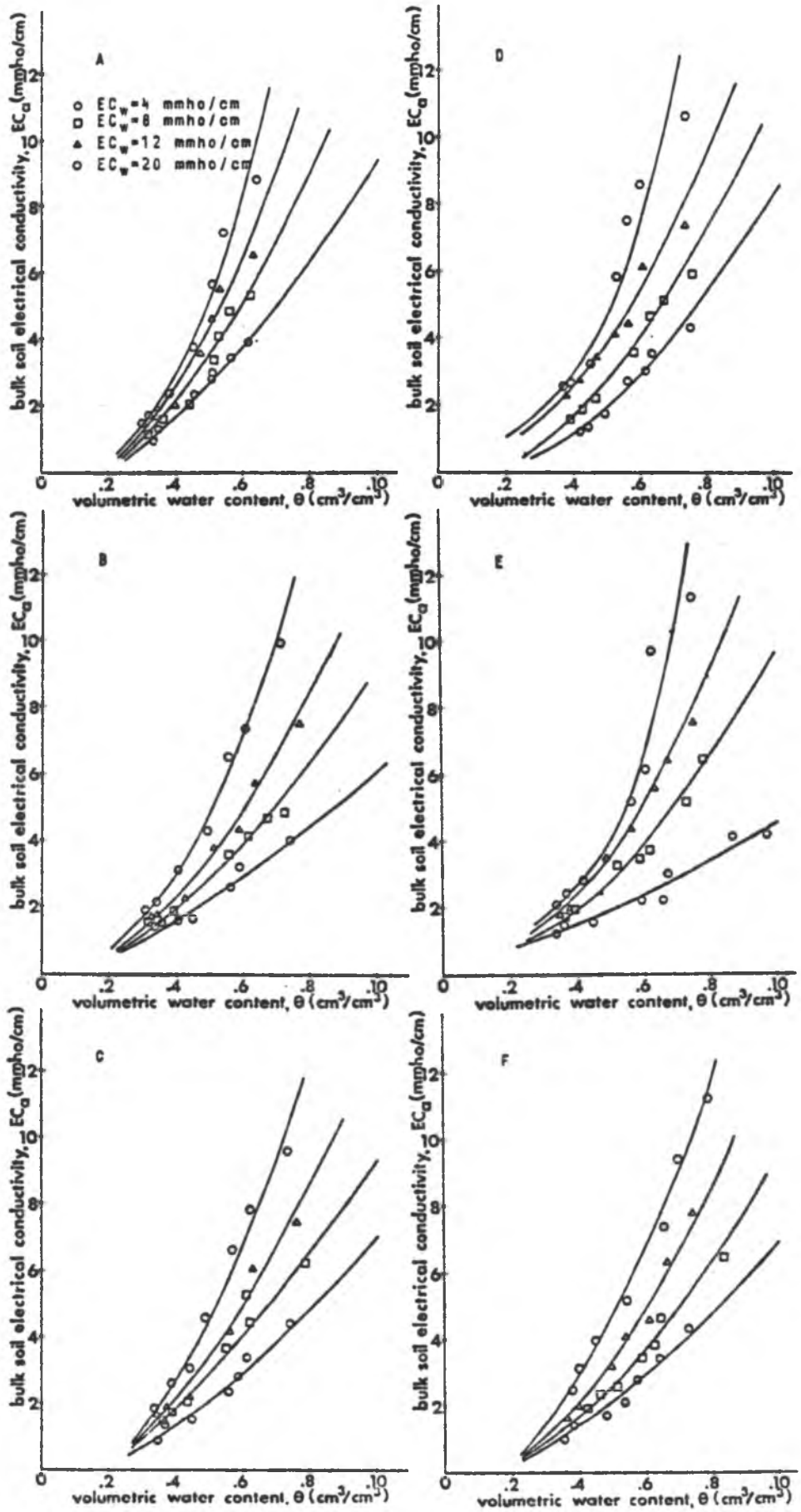


Fig. 4. Plots of bulk soil electrical conductivity, EC_a, vs. soil volumetric water content, θ, for Kukaiau Series at different exchangeable sodium percentage (ESP).

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

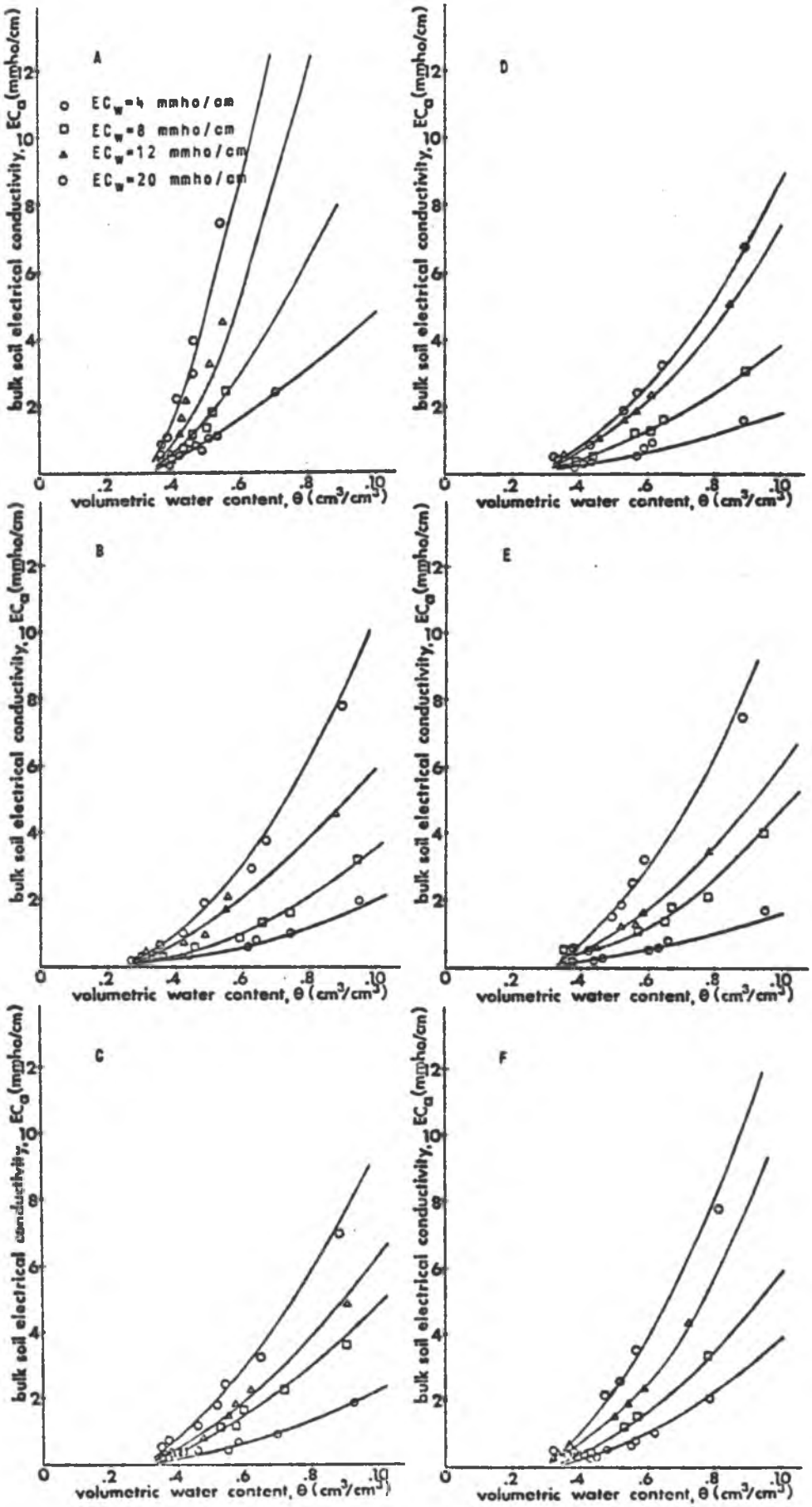
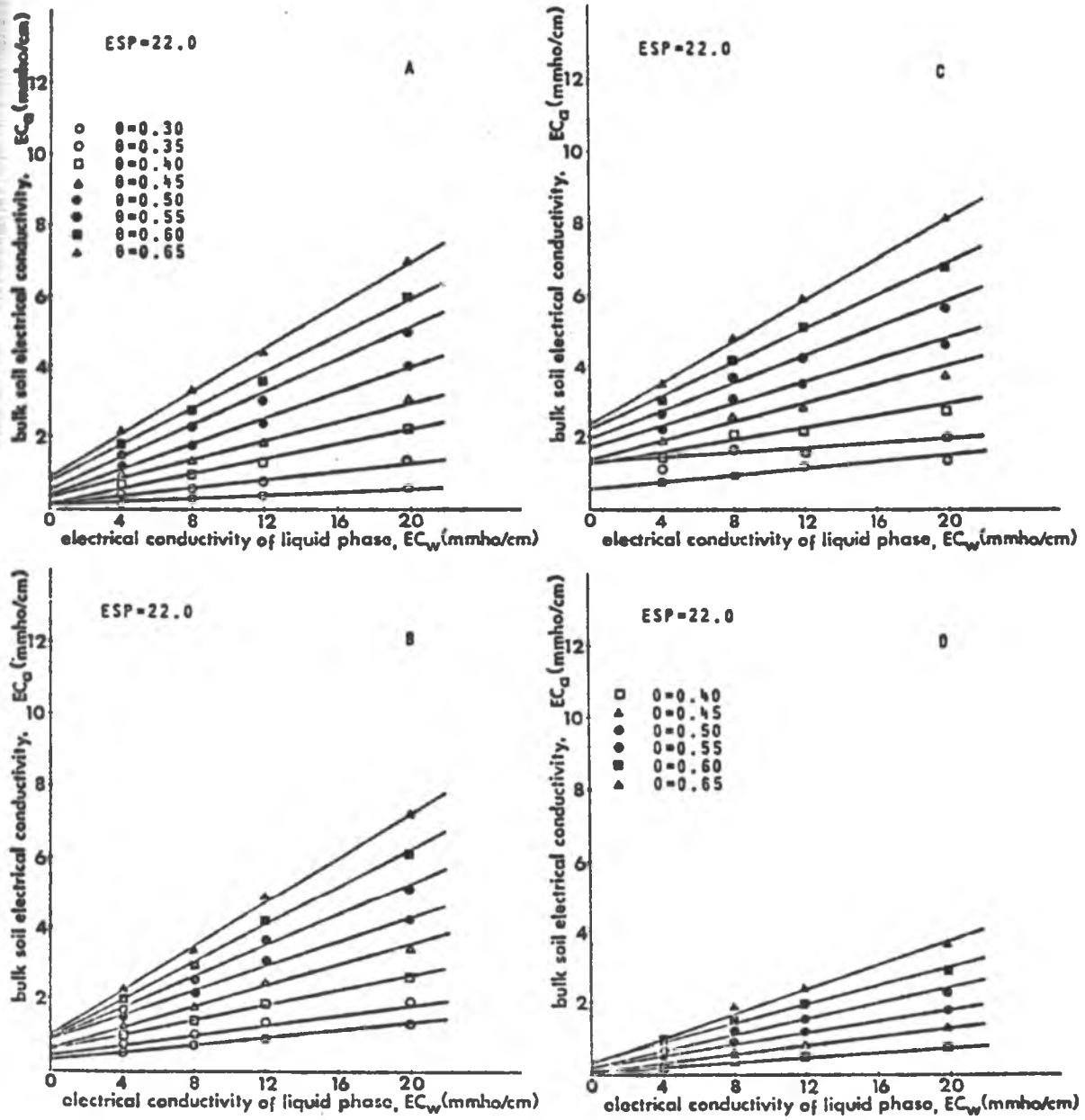


Fig. 5. Plots of bulk soil electrical conductivity (EC_a) vs. liquid-phase elctrical conductivity (EC_w) at various soil volumetric water content (θ) for the four soils at the ESP = 22.0 showing the extrapolated value of specific surface conductivity (EC_s).

A. Kawaihae Series
B. Molokai Series
C. Lualualei Series
D. Kukaiau Series



intercept on the EC_a-axis of the graph relating EC_a to EC_w. For the estimation of the specific surface conductivity, the linear regression technique was used to extrapolate each line to $EC_w = 0$. As shown in Fig. 5, a common intercept on the y-axis from lines at various θ was not obtained. The overall data of the y-axis intercepts obtained by extrapolating EC_a vs. EC_w to $EC_w = 0$ at different θ for each soil at different ESP levels are presented in Tables 11, 12, 13 and 14. In general, the y-axis intercepts were larger from lines representing EC_a vs. EC_w at higher water content (θ). Rhoades et al. (1976) in a similar study on four California soils also obtained a similar situation; however, no details were disclosed on how the data were used to derive single EC_s values for their soils. A close analysis of their data on Indio V.F.S.L. revealed that the estimated EC_s (0.25 mmho/cm) approximately corresponded to the intercept on the y-axis resulting from extrapolating EC_s vs. EC_w at $\theta = 30$. In this study, the estimation of EC_s of various soils was done in the following manner: A range of EC_s was obtained by averaging the y-axis intercepts for a range of θ of 50-30, 45-30%, 40-30%, 35-30% and 30%, respectively and the results were shown in Tables 15, 16, 17 and 18. In general, the EC_s values decrease as the range of θ from which the average is taken becomes narrower. The threshold water content (θ_t) which was evaluated by -b/a, was then employed to estimate the approximate specific surface conductivity values of each soil. The constant a and b in eq. (6) were determined by rearranging eq. (5) in order to isolate T, the soil pore geometry or transmission coefficient. Then, we have

$$T = \frac{EC_a - EC_s}{EC_w - \theta} \qquad (20)$$

Table 11. Relationship between soil volumetric water content, θ, and extrapolated specific surface conductivity, EC_S, for Kawaihae Series at different ESP levels

VOLUMETRIC WATER CONTENT	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
	MMHO/CM					
60	0.9000	0.2700	0.6100	0.9400	1.2100	1.0300
55	1.0200	0.2300	0.4900	0.5900	0.9900	0.7600
50	0.8700	0.2400	0.3000	0.4400	0.6800	0.8900
45	0.5100	0.2200	0.2400	0.2900	0.4900	0.6300
40	0.4100	0.1700	0.1200	0.2300	0.2300	0.3400
35	0.5200	0.1300	0.0240	0.1600	0.0470	0.0650
30	0.3100	0.0380	0.0400	0.0710	0.0640	0.0150

Table 12. Relationship between soil volumetric water content, θ, and extrapolated specific surface conductivity, EC_s, for Molokai Series at different ESP levels .

VOLUMETRIC WATER CONTENT	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
	MMHO/CM					
60	0.6000	0.2100	0.8800	0.2200	1.0300	0.7100
55	0.5600	0.1500	0.8000	0.1800	0.9600	0.6800
50	0.5200	0.0640	0.8100	0.1400	0.6600	0.8100
45	0.4800	0.0280	0.6500	0.1100	0.5100	0.7100
40	0.4500	0.0230	0.4900	0.1000	0.3500	0.5700
35	0.3700	0.0210	0.3400	0.1100	0.2700	0.4000
30	0.2800	0.0330	0.2100	0.0930	0.2100	0.2600

Table 13. Relationship between soil volumetric water content, θ, and extrapolated specific surface conductivity, EC_s, for Lualualei Series at different ESP levels

VOLUMETRIC WATER CONTENT	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
	MMHO/CM					
60	2.8700	1.6400	2.1500	1.3600	1.6700	1.9100
55	2.5400	1.6300	1.9200	1.6100	1.8000	1.5700
50	2.2000	1.5500	1.6600	1.3600	1.6900	1.3700
45	1.8400	1.4500	1.4100	1.1100	1.5300	1.1000
40	1.5300	1.3000	1.1800	0.8600	1.3300	0.9300
35	1.1100	1.1800	1.3400	0.5600	1.1500	0.6900
30	0.6700	1.0600	0.5500	0.3500	1.0000	0.5400

Table 14. Relationship between soil volumetric water content, θ, and extrapolated specific surface conductivity, EC_s, for Kukaiau Series at different ESP levels

VOLUMETRIC WATER CONTENT	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
	MMHO/CM					
60	0.0340	0.1100	0.2300	0.2300	0.5100	0.1900
55	0.0100	0.0540	0.1400	0.2400	0.1400	0.0930
50	0.0140	0.0560	0.0800	0.1800	0.1500	0.0310
45	0.0110	0.0400	0.0140	0.1300	0.0910	0.0029
40	-0.0030	0.0430	0.0540	0.1300	0.1600	0.0011

Table 15. Relationship between mean specific surface conductivity, EC_s, and threshold water content, θ_t, for Kawaihae Series at different ESP levels

VOLUMETRIC WATER CONTENT	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
	MMHO/CM					
50-30	0.520*/ / 24.74	0.160 / 21.46	0.140 / 26.98	0.240 / 29.70	0.300 / 34.74	0.390 / 35.18
45-30	0.440 / 20.87	0.140 / 19.70	0.110 / 23.70	0.190 / 45.07	0.210 / 28.96	0.260 / 31.44
40-30	0.410 / 18.30	0.110 / 17.64	0.061 / 19.86	0.150 / 21.46	0.110 / 21.80	0.140 / 29.81
35-30	0.420 / 18.94	0.084 / 16.98	0.032 / 15.74	0.120 / 19.72	0.056 / 15.74	0.040 / 24.74
30	0.310 / 16.43	0.038 / 15.60	0.040 / 17.32	0.071 / 15.73	0.064 / 17.27	0.015 / 20.63

*/Specific surface conductivity/threshold water content,

Table 16. Relationship between mean specific surface conductivity, ECs, and threshold water content, θ_t, for Molokai Series at different ESP levels

VOLUMETRIC WATER CONTENT	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
	MMHO/CM					
50-30	0.420 */ 31.77	0.034 16.14	0.500 34.42	0.110 17.34	0.400 29.40	0.550 33.84
45-30	0.400 30.14	0.026 24.48	0.420 28.70	0.100 16.24	0.340 24.17	0.390 27.64
40-30	0.370 24.40	0.026 24.48	0.350 22.31	0.100 16.24	0.280 21.74	0.410 30.07
35-30	0.330 19.40	0.027 25.10	0.280 18.12	0.100 16.24	0.240 19.81	0.330 26.10
30	0.280 16.43	0.033 15.60	0.210 13.49	0.093 14.93	0.210 14.38	0.260 20.54

*/ Specific surface conductivity/threshold water content.

Table 17. Relationship between mean specific surface conductivity, EC_s, and threshold water content, θ_t, for Lualualei Series at different ESP levels

VOLUMETRIC WATER CONTENT	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
	MMHO/CM					
30-30	1.470 */ 40.31	1.310 34.84	1.230 32.80	0.850 25.19	1.340 29.05	0.930 24.16
45-30	1.290 36.54	1.250 30.72	1.120 29.78	0.720 22.10	1.250 26.48	0.820 21.87
40-30	1.100 32.10	1.180 26.41	1.020 23.23	0.590 18.06	1.160 23.87	0.720 19.01
35-30	0.890 25.43	1.120 23.17	0.950 21.48	0.460 16.84	1.080 21.64	0.620 17.43
30	0.670 20.62	1.060 20.89	0.550 14.19	0.350 14.19	1.000 19.54	0.540 14.16

*/Specific surface conductivity/threshold water content.

Table 18. Relationship between mean specific surface conductivity, EC_s, and threshold water content, θ_t, for Kukaiau Series at different ESP levels.

VOLUMETRIC WATER CONTENT	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
	MMHO/CM					
60-40	0.013*/ / 38.17	0.062 / 30.14	0.100 / 31.53	0.180 / 33.46	0.210 / 31.41	0.064 / 36.17
55-40	0.008 / 36.43	0.050 / 29.06	0.072 / 30.02	0.170 / 32.10	0.140 / 22.04	0.032 / 33.14
50-40	0.007 / 36.06	0.048 / 28.16	0.049 / 26.75	0.150 / 30.08	0.130 / 22.17	0.012 / 33.00
45-40	0.004 / 35.08	0.044 / 25.84	0.034 / 22.70	0.130 / 26.87	0.130 / 22.17	0.002 / 30.08
40	-0.003 / 33.55	0.043 / 25.98	0.054 / 23.25	0.130 / 26.87	0.160 / 25.04	0.001 / 30.00

*/Specific surface conductivity/threshold water content.

By using the original data points given in Figs. 1, 2, 3 and 4 and the corresponding EC_s values established above, T was evaluated. Since T is equal to $a\theta + b$ as given by eq. (6), the plotting of T vs. θ and with the use of the linear regression analysis would give rise to a and b simultaneously. An example was given in Fig. 6 on Kawaihae Series. The threshold water content (θ_t) was then determined. Different θ_t values were established by incorporating different mean EC_s values at various soil moisture ranges into eq. (20). The results are presented in Tables 15, 16, 17 and 18. The threshold water content generally decreases with decreasing specific surface conductivity at each soil ESP level. By extrapolating the curves (EC_a vs. θ) in Figs. 1, 2, 3 and 4 to $EC_a = 0$, it was roughly estimated that the Molokai Series would exhibit no EC_a measurement below a water content of 20%. Experience in both field and laboratory works also confirmed this finding. Therefore the threshold water content established mathematically for Molokai Series would not be expected to exceed the above amount. When referred back to Table 16, the θ_t established by using the EC_s values from the soil water content of 30% at all soil ESP levels appeared to be the best fitted to the above observation. For this reason, the soil water content of 30% was arbitrarily taken to determine the specific surface conductivity of the Molokai Series. The same reasoning was applied to Kawaihae, Lualualei and Kukaiau Series whereby the corresponding water content from which the specific surface conductivity was determined was 30, 30 and 40%, respectively.

The mean specific surface conductivity data (Table 19) together with the information on the particle-size distribution of the four

Fig. 6. Relationship between transmission coefficient, T, and soil volumetric water content, θ, for Kawaihae Series at different exchangeable sodium percentage levels.

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

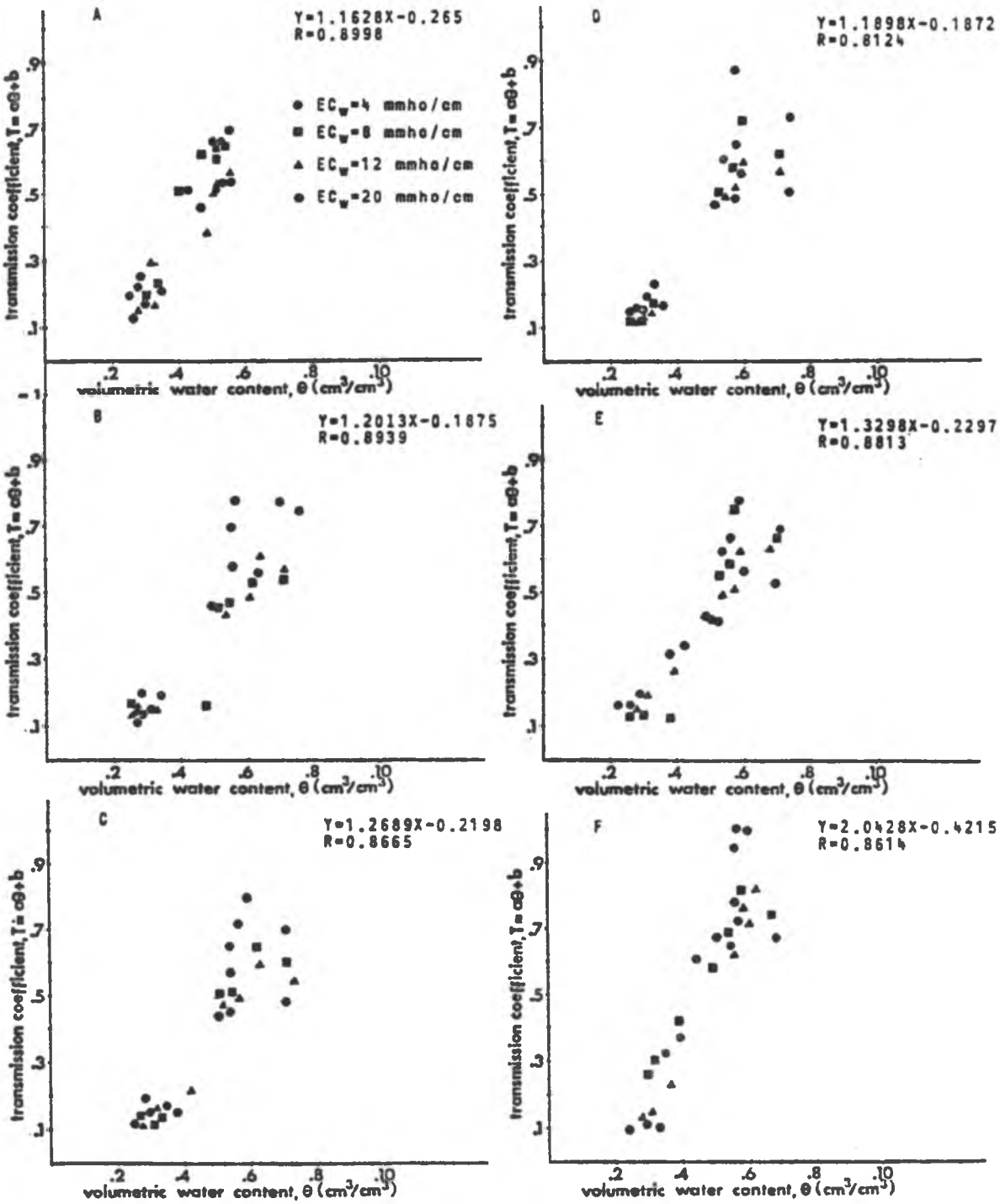

A
Y=1.1628X-0.265
R=0.8998
● EC_w=4 mmho/cm
■ EC_w=8 mmho/cm
▲ EC_w=12 mmho/cm
● EC_w=20 mmho/cm
D
Y=1.1898X-0.1872
R=0.8124
B
Y=1.2013X-0.1875
R=0.8939
E
Y=1.3298X-0.2297
R=0.8813
C
Y=1.2689X-0.2198
R=0.8665
F
Y=2.0428X-0.4215
R=0.8614
transmission coefficient, T = aθ+b
volumetric water content, θ (cm³/cm³)

Table 19. Specific surface conductivity (EC_s) of the selected soils at various soil ESP

SERIES	EXCHANGEABLE SODIUM PERCENTAGE						
	0.0	11.89	22.02	36.60	59.39	100.00	AVE
	MMHO/CM						
KAWAIHAE	0.31A */	0.04B	0.04B	0.07B	0.06B	0.02B	0.09
MOLOKAI	0.28A	0.03C	0.21AB	0.09BC	0.21AB	0.28A	0.28
LUALUALEI	0.67AB	1.06A	0.55B	0.35B	1.00A	0.54B	0.70
KUKAIAU	0.0 C	0.04BC	0.05BC	0.13AB	0.16A	0.0 C	0.06

*/Means followed by a common letter are not significantly different at the 5% level tested by the Duncan Multiple Range Test.

soils (Table 8) demonstrated that specific surface conductivity was larger for finer-texture soil as expected and previously confirmed by Rhoades et al. (1976). Since the Lualualei Series is enriched in clay-size and montmorillonitic particles, it is not surprising that its mean specific surface conductivity is the highest among the four soils. The mean specific surface conductivity of the four soils is in the order of

Lualualei > Molokai > Kawaihae > Kukaiau

When referring to the mineralogical composition of the soils, the above order is consistent with that of the specific surface conductivity established for various standard clay minerals and synthetic sesquioxides in the latter part of this study. As shown by eq. (5), under identical conditions of EC_w, θ and T, a larger EC_s would result in a correspondingly higher EC_a reading. Therefore in soils with a roughly similar mineralogical composition, the one which possesses the highest content of clay-size particles would have the largest bulk soil electrical conductivity provided all other variables are constant.

The plots of EC_a vs. EC_w at various θ and soil ESP for each soil series were normalized by using the pre-determined appropriate EC_s values and the graphs are presented in Figs. 7, 8, 9 and 10. Generally, the positive linear relationship between EC_a and EC_w at each θ predicted by eq. (5), (18) and (19) was not observed at high soil water content. The higher the soil water content, the greater was the deviation from linearity between EC_a and EC_w.

The correlation coefficient (r), which was obtained along with a and b by the linear regression analysis of T vs. θ, determined the

Fig. 7. Relationship between bulk soil electrical conductivity, EC_a, liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for Kawaihae Series at different exchangeable sodium percentage levels.

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

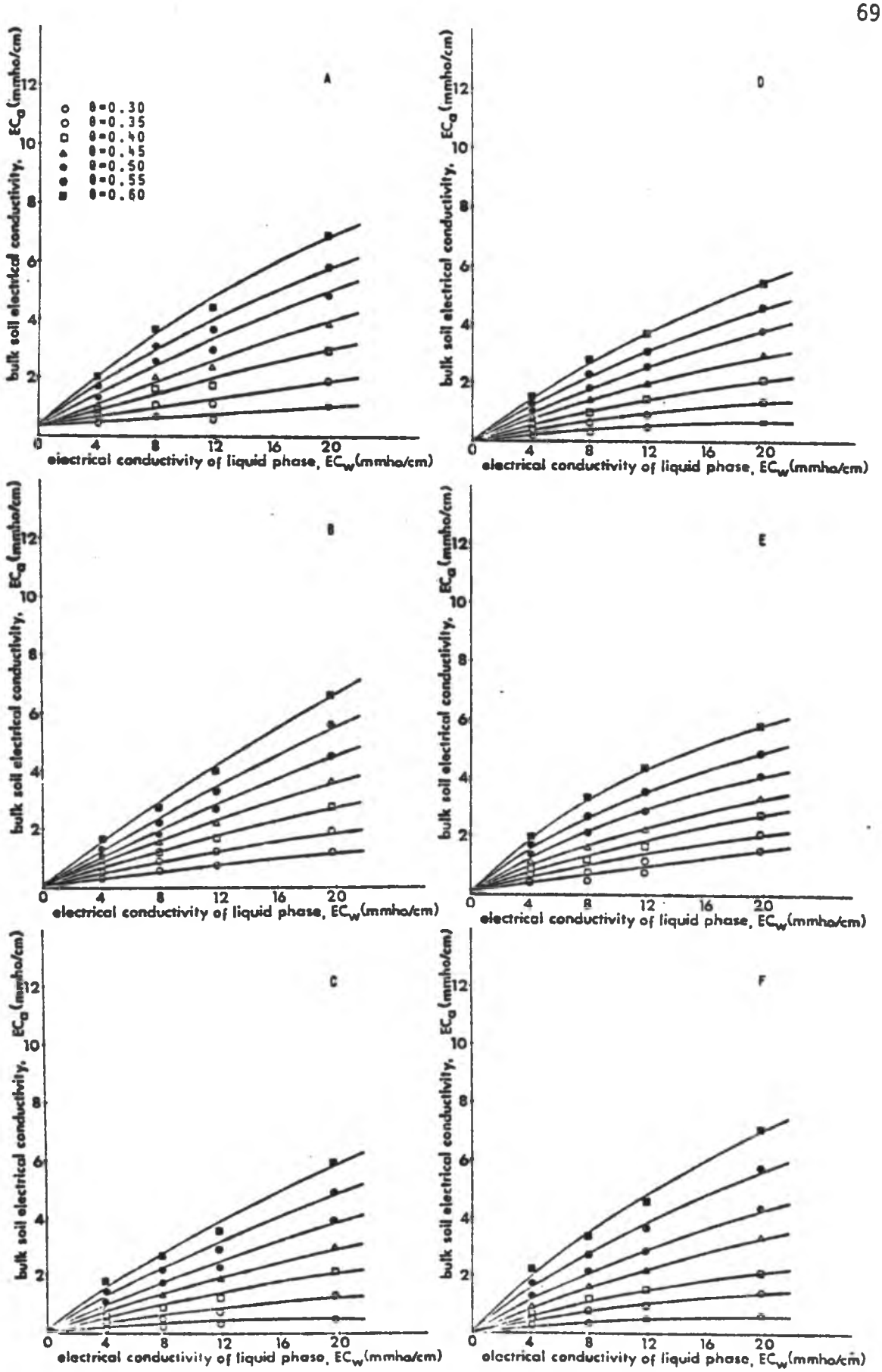


Fig. 8. Relationship between bulk soil electrical conductivity, EC_a, liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for Molokai Series at different exchangeable sodium percentage levels.

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

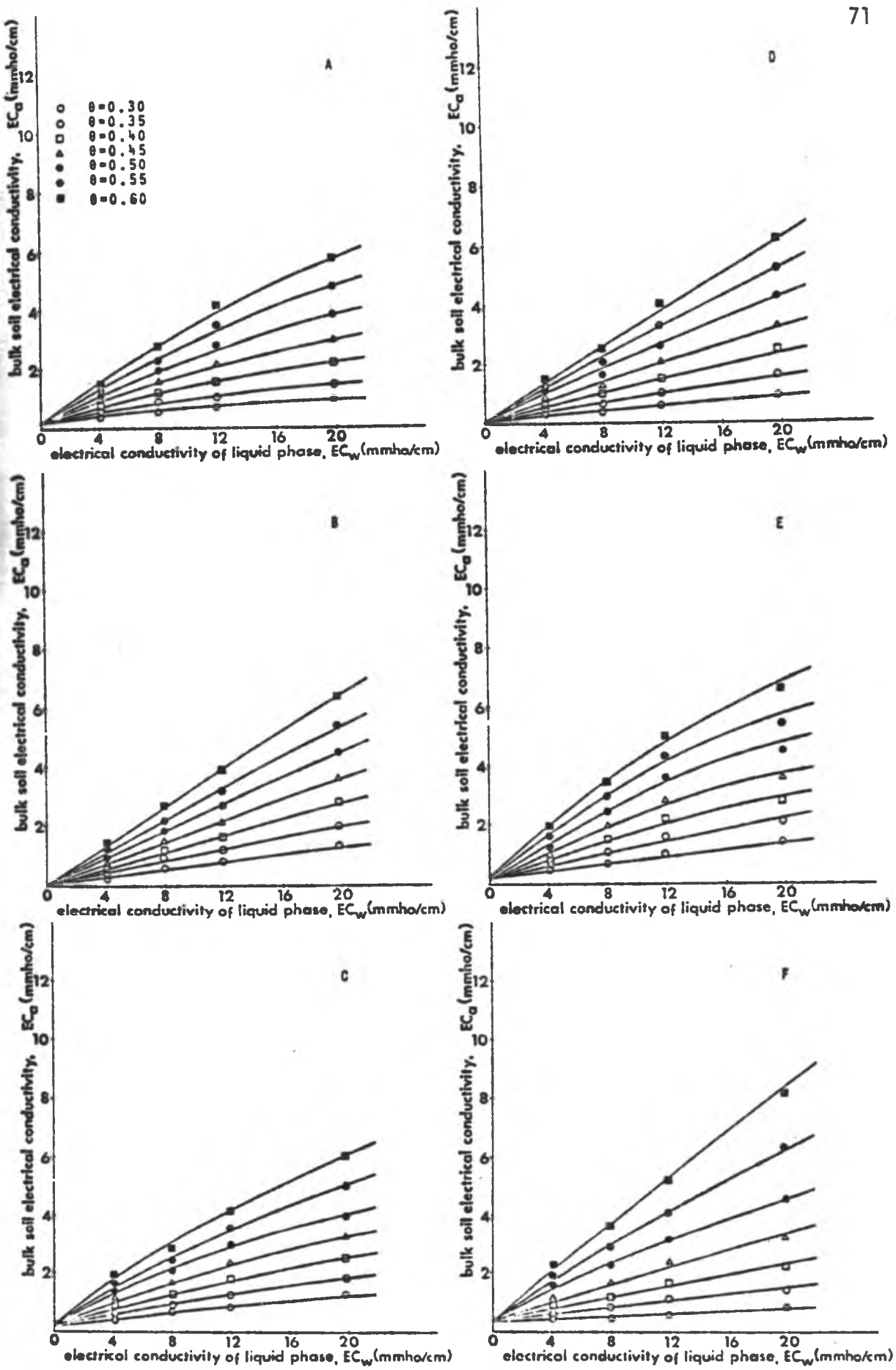


Fig. 9. Relationship between bulk soil electrical conductivity, EC_a, liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for Lualualei Series at different exchangeable sodium percentage levels.

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

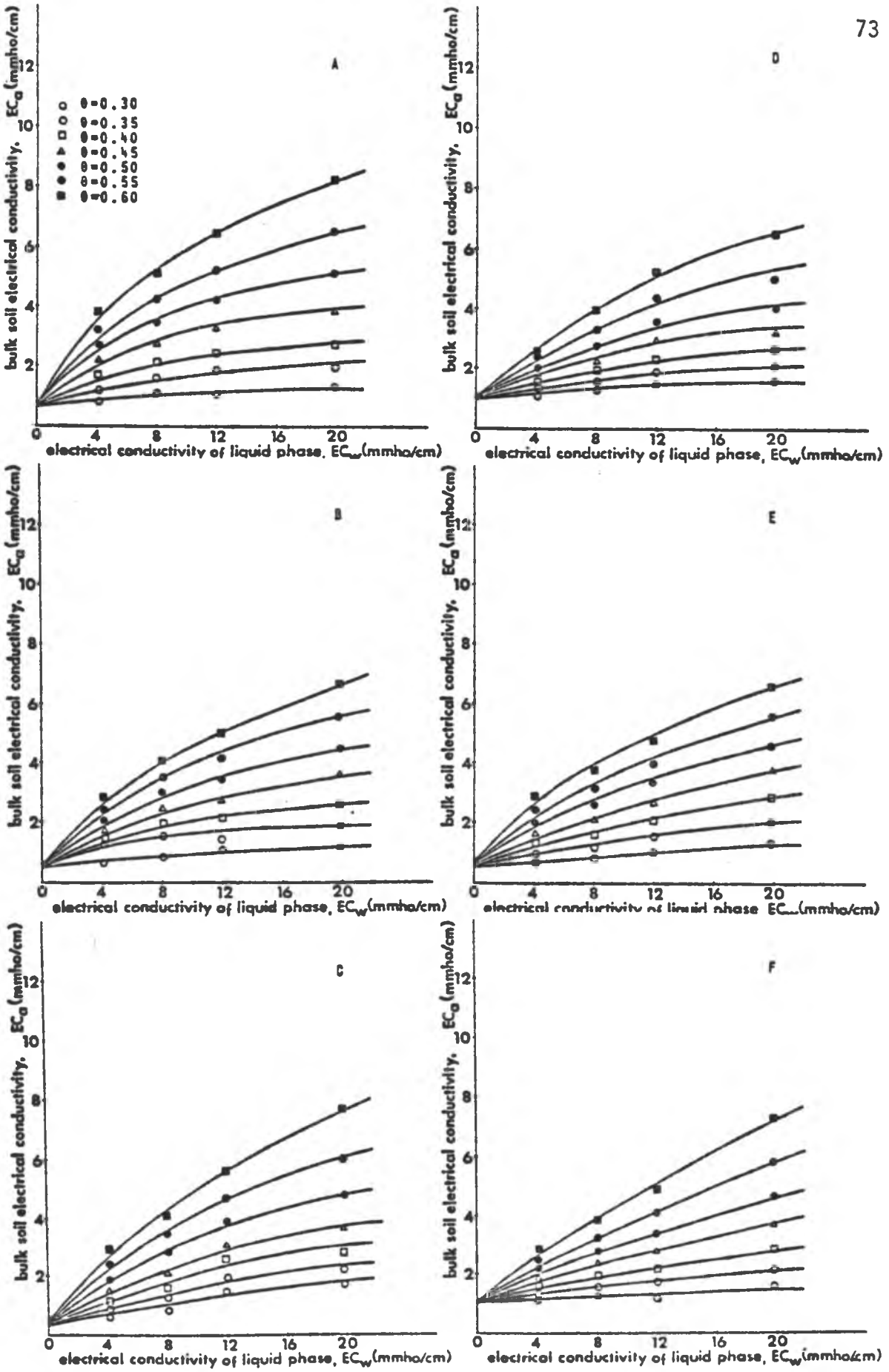
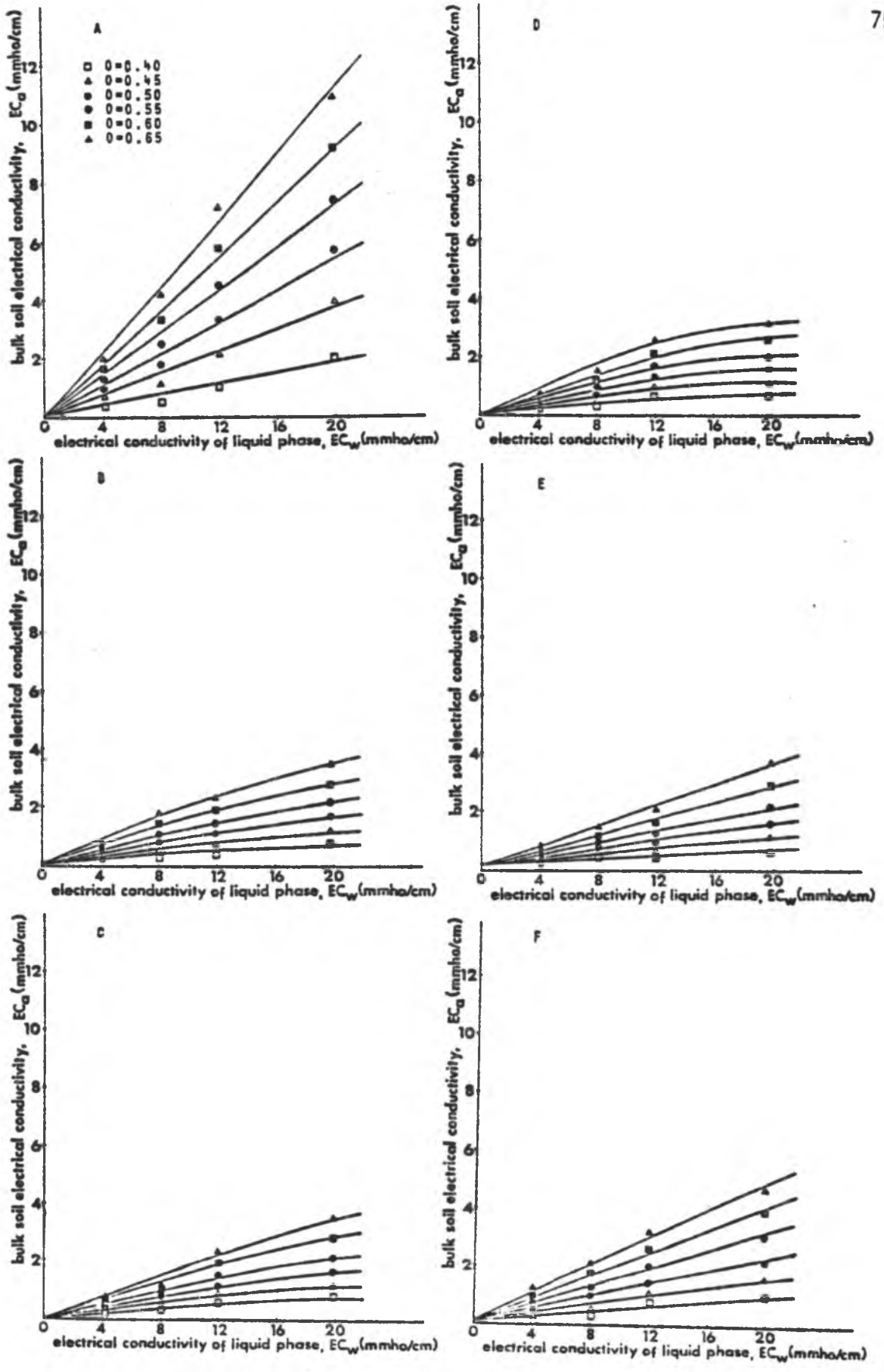

A
B
C
D
E
F
θ=0.30
θ=0.35
θ=0.40
θ=0.45
θ=0.50
θ=0.55
θ=0.60
bulk soil electrical conductivity, EC_a (mmho/cm)
electrical conductivity of liquid phase, EC_w (mmho/cm)
0
2
4
6
8
10
12
16
20

Fig. 10. Relationship between bulk soil electrical conductivity, EC_a, liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for Kukaiau Series at different exchangeable sodium percentage levels.

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0



adequacy of using eq. (5) in predicting the behavior of EC_a in response to changing θ, EC_w and EC_s. The mean r value established for Lualualei Series over all the soil ESP levels was the lowest among the four soils (Table 22). This indicates that, in comparison with the other soils, eq. (5) describes less adequately the dependence of EC_a of this soil on θ and EC_w when θ is above the threshold value. The unstable structural properties of the Lualualei Series as well as its swelling and shrinkage upon wetting and drying has likely caused a changing soil bulk density in the core sample which in turn affected the EC_a measurements.

Effects of liquid-phase electrical conductivity (EC_w) and soil volumetric water content (θ) on the rate of change of bulk soil electrical conductivity with respect to soil volumetric water content ($dEC_a/d\theta$)

When eq. (19) is differentiated with respect to θ, we have,

$$dEC_a/d\theta = 2\ (EC_w)(a)(\theta) + (EC_w)(b) \qquad (21)$$

Eq. (21) predicts that the change of EC_a per unit change of θ is a function of θ and EC_w. The rate of change of EC_a with respect to θ at various EC_w and soil ESP of each soil was obtained by substituting appropriate values into eq. (21). The plotting of $dEC_a/d\theta$ vs. EC_w at each θ and soil ESP for each soil verified the prediction of eq. (21), that $dEC_a/d\theta$ increases linearly with increasing EC_w and θ. The results are shown in Figs. 11, 12, 13 and 14. The rate of change of EC_a with respect to θ among the four soils is generally in the following order:

Lualualei > Molokai > Kawaihae > Kukaiau

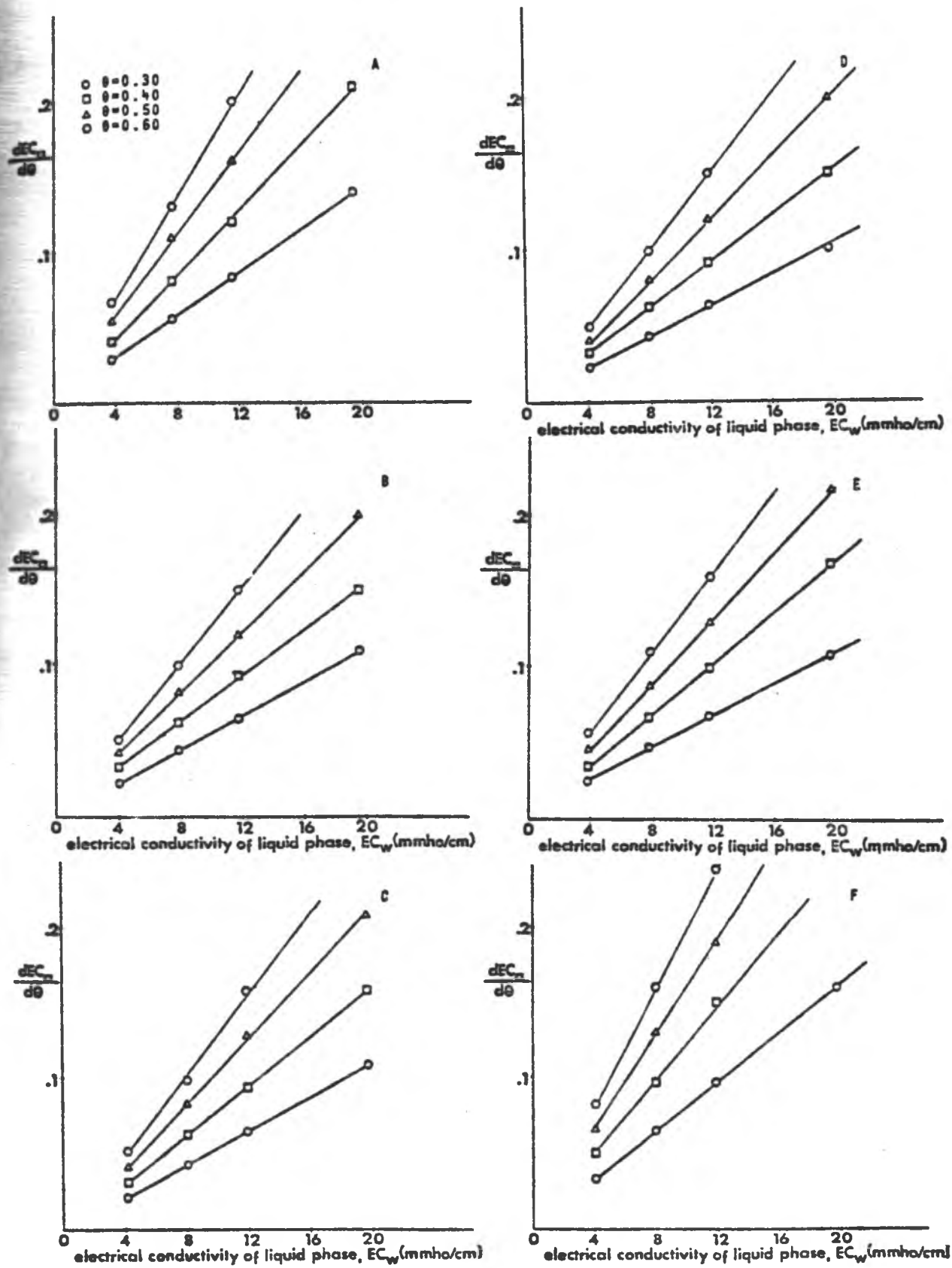


Fig. 12. Dependence of $dEC_a/d\theta$ on soil solution electrical conductivity (EC_w) and soil volumetric water content (θ) for Molokai Series.

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

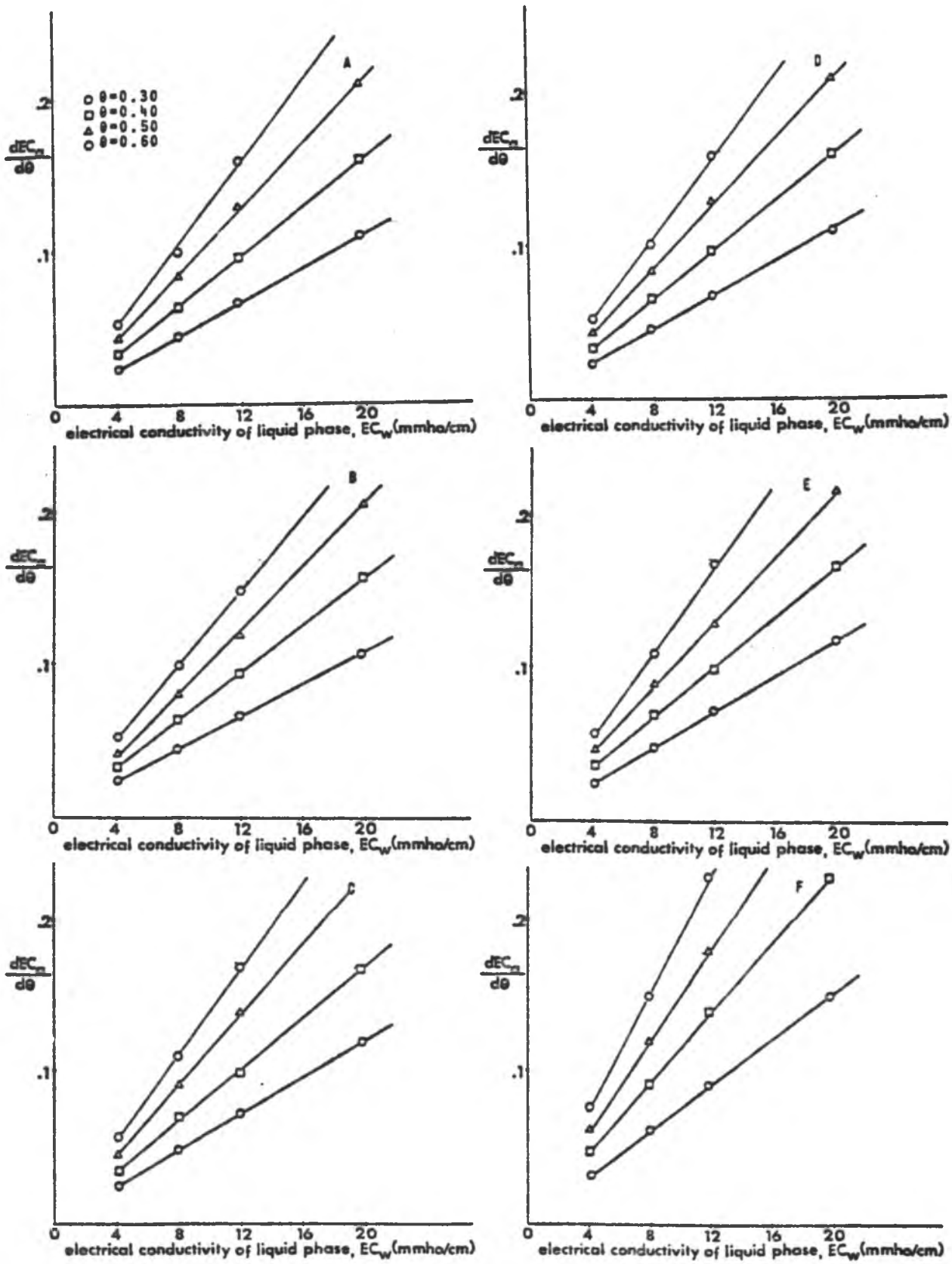


Fig. 13. Dependence of $dEC_a/d\theta$ on soil solution electrical conductivity (EC_w) and soil volumetric water content (θ) for Lualualei Series.

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0

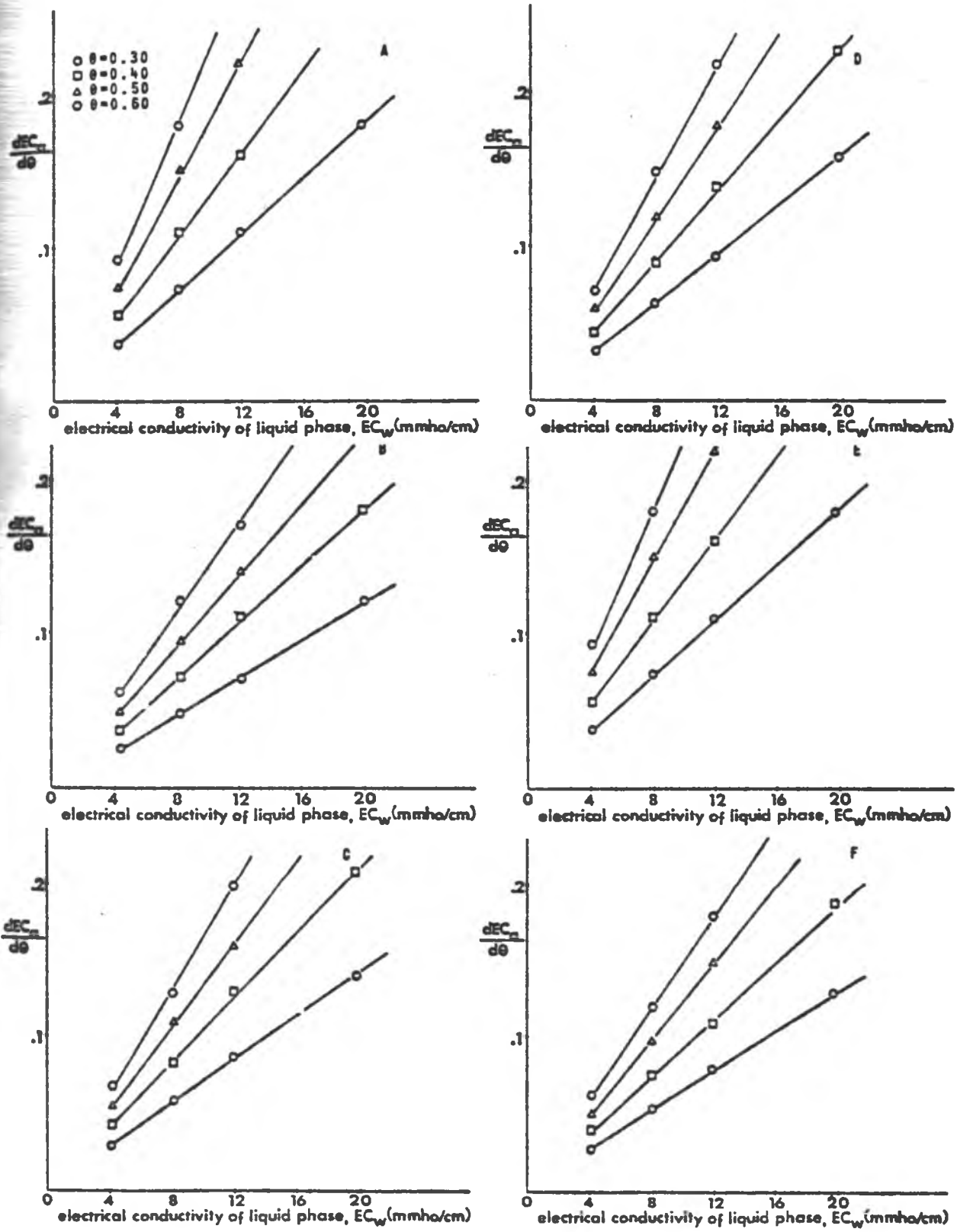
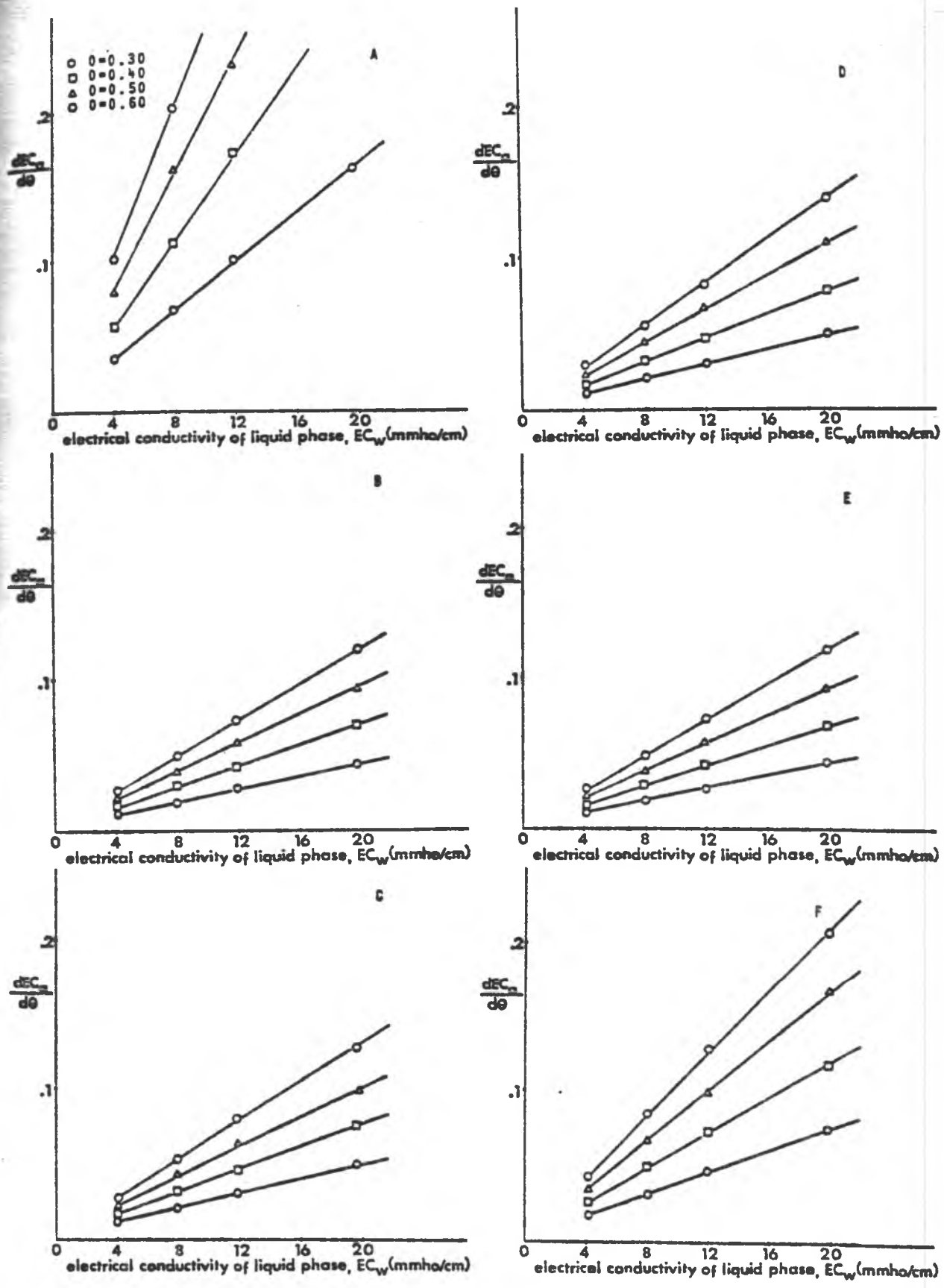


Fig. 14. Dependence of $dEC_a/d\theta$ on soil solution electrical conductivity (EC_w) and soil volumetric water content (θ) for Kukaiau Series.

A. ESP = 0.0
B. ESP = 11.9
C. ESP = 22.0
D. ESP = 36.6
E. ESP = 59.4
F. ESP = 100.0


A
B
C
D
E
F
θ=0.30
θ=0.40
θ=0.50
θ=0.60
dEC_a/dθ
.1
.2
0
4
8
12
16
20
electrical conductivity of liquid phase, EC_w(mmho/cm)

The effect of soil exchangeable sodium percentage (ESP) on bulk soil electrical conductivity (EC_a) and other related parameters

The influence of soil ESP at various θ and EC_w on bulk soil electrical conductivity (EC_a) for the four soils is presented in Figs. 15, 16, 17 and 18. The statistical analysis of the data for each soil is shown in Tables 30, 31, 32 and 33 in Appendix C. The Ca-saturated Kukaiau Series possesses a much greater EC_a than those of the other ESP levels. This phenomenon is more pronounced at high θ and EC_w . The Kawaihae and Lualualei Series also demonstrated similar trends but with a smaller magnitude. As will be shown from suspension measurements, this is contrary to expectation. The comparatively large EC_a exhibited by the Ca-saturated Kukaiau Series can be attributed to the artifact due to core differences and the presence of more mass in less swollen soil (higher bulk density). The swelling which occurred in the Na-saturated soil decreased the bulk density of the core sample thus lowering the bulk soil electrical conductivity. Of the four soils under investigation in this study, the effect of Na treatment in terms of bulk soil electrical conductivity was the greatest in Kukaiau Series.

In order to demonstrate the effect of core differences and swelling on the bulk soil electrical conductivity, a swelling soil (Lualualei Series) and a non-swelling soil (Molokai Series) were chosen. Each of these soils were packed into two different cores (A and B) according to their field bulk density. The core samples were then leached with pure $CaCl_2$ and NaCl solutions of various concentrations (concentrations were 4.0, 8.0, 12.0 and 20.0 mmho/cm, respectively) and the bulk soil electrical conductivity was measured at each concentration at

Fig. 15. Response of bulk soil electrical conductivity (EC_a) to soil exchangeable sodium percentage (ESP) on various liquid-phase electrical conductivity (EC_w) and soil volumetric water content (θ) for Kawaihae Series.

A. $\theta = 0.30$
B. $\theta = 0.40$
C. $\theta = 0.50$
D. $\theta = 0.60$

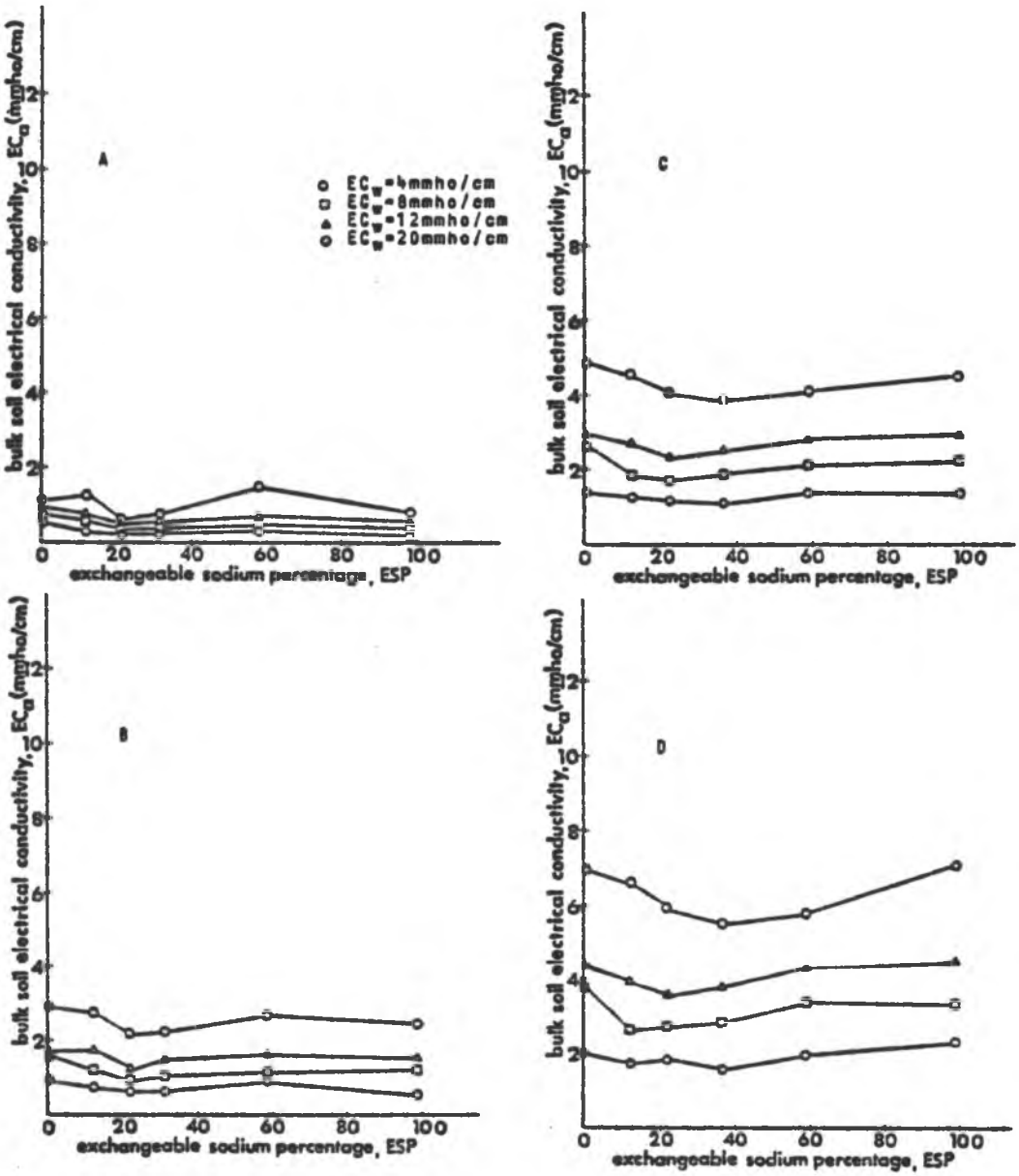

A
B
C
D
bulk soil electrical conductivity, EC_a (mmho/cm)
exchangeable sodium percentage, ESP
0
20
40
60
80
100
2
4
6
8
10
12
EC$_w$=4mmho/cm
EC$_w$=8mmho/cm
EC$_w$=12mmho/cm
EC$_w$=20mmho/cm

Fig. 16. Response of bulk soil electrical conductivity (EC_a) to soil exchangeable sodium percentage (ESP) on various liquid-phase electrical conductivity (EC_w) and soil volumetric water content (θ) for Molokai Series.

A. $\theta = 0.30$
B. $\theta = 0.40$
C. $\theta = 0.50$
D. $\theta = 0.60$

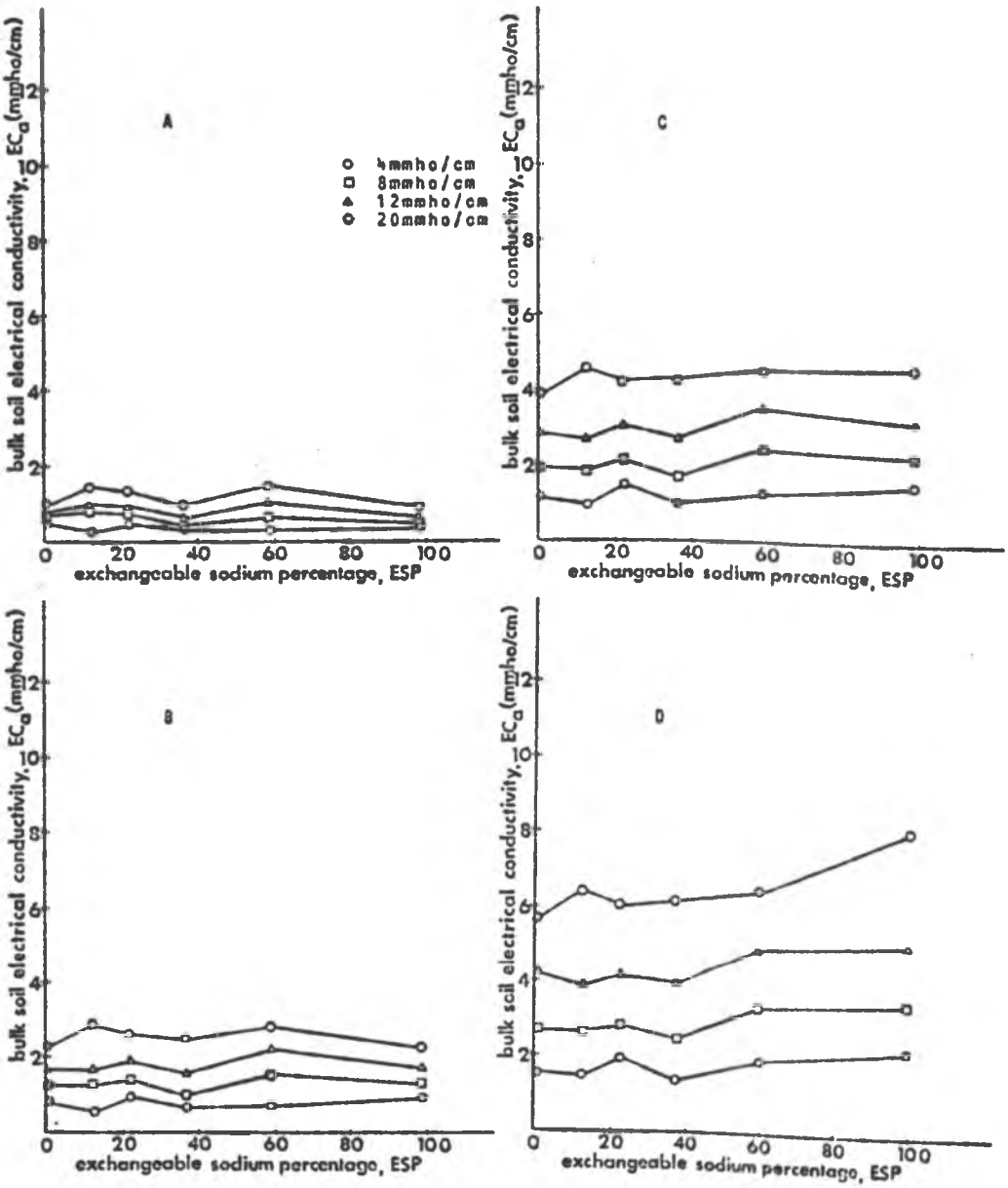

A
B
C
D
4mmho/cm
8mmho/cm
12mmho/cm
20mmho/cm
bulk soil electrical conductivity, EC_a (mmho/cm)
exchangeable sodium percentage, ESP
0
20
40
60
80
100
2
4
6
8
10
12

Fig. 17. Response of bulk soil electrical conductivity (EC_a) to soil exchangeable sodium percentage (ESP) on various liquid-phase electrical conductivity (EC_w) and soil volumetric water content (θ) for Lualualei Series.

A. $\theta = 0.30$
B. $\theta = 0.40$
C. $\theta = 0.50$
D. $\theta = 0.60$

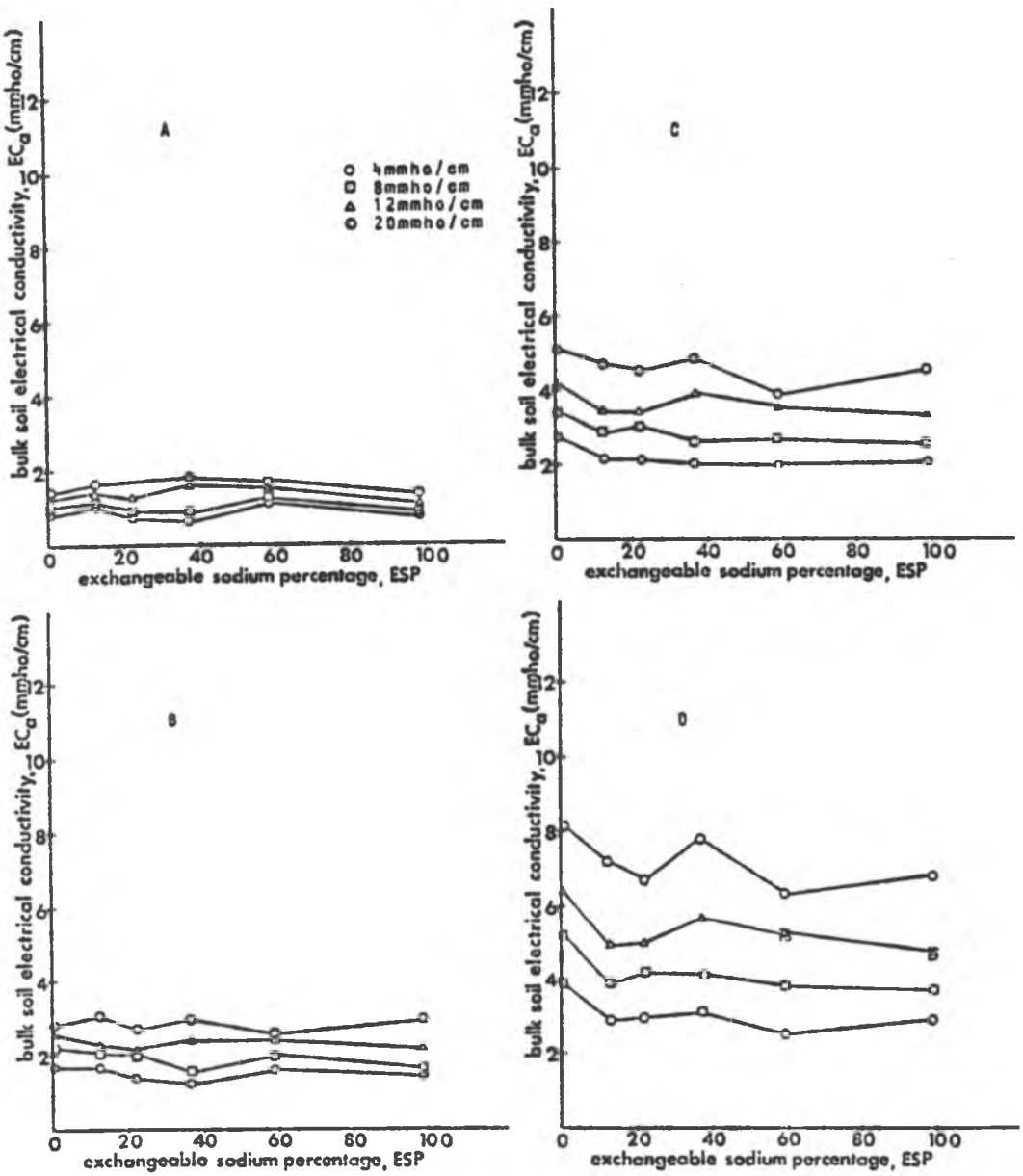
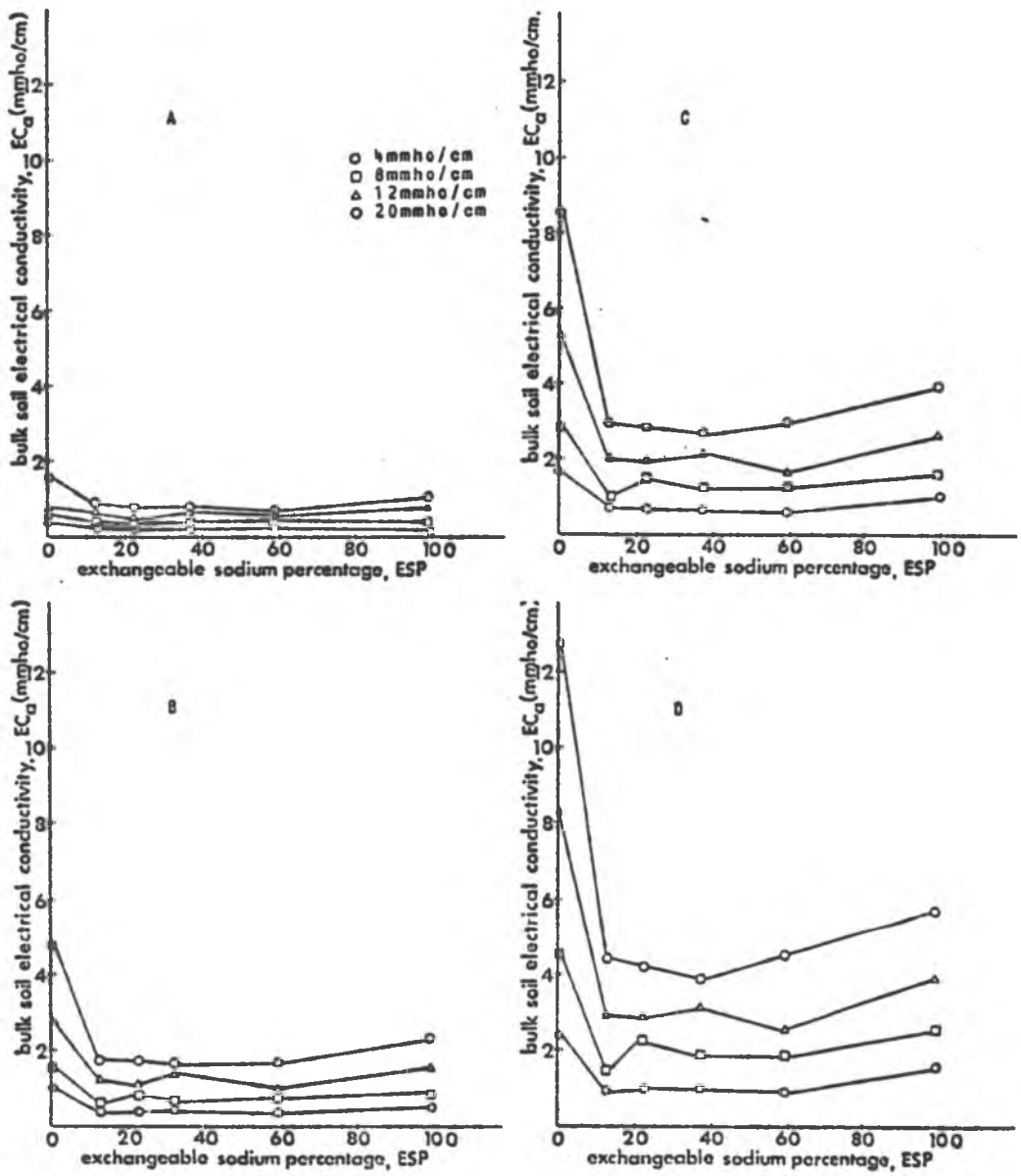

A
B
C
D
4mmho/cm
8mmho/cm
12mmho/cm
20mmho/cm
bulk soil electrical conductivity, EC_a (mmho/cm)
exchangeable sodium percentage, ESP
0
20
40
60
80
100
2
4
6
8
10
12

Fig. 18. Response of bulk soil electrical conductivity (EC_a) to soil exchangeable sodium percentage (ESP) on various liquid-phase electrical conductivity (EC_w) and soil volumetric water content (θ) for Kukaiau Series.

A. $\theta = 0.40$
B. $\theta = 0.50$
C. $\theta = 0.60$
D. $\theta = 0.70$


A
B
C
D
4mmho/cm
8mmho/cm
12mmho/cm
20mmho/cm
bulk soil electrical conductivity, EC_a (mmho/cm)
exchangeable sodium percentage, ESP
0
20
40
60
80
100
2
4
6
8
10
12

saturation. The results are presented in Tables 29 and 30 in Appendix E. It is obvious that core differences do affect bulk soil electrical conductivity as indicated by the differences in the y-intercepts (specific surface conductivity, EC_s). The higher average specific surface conductivity possessed by the Ca-saturated Lualualei Series over that of the Na counterpart further indicated that swelling decreases bulk soil electrical conductivity through the lowering of the soil bulk density. However in the Molokai Series, since little or no swelling had resulted upon Na-saturation, an opposite trend was observed in the average specific surface conductivity values. This was consistent with the suspension data on standard clay minerals presented in the latter part of this thesis.

The effect of soil ESP on other related parameters such as EC_s, θ_t -b/a, and r does not appear clearly predictable as shown by the statistical analysis in Tables 20, 21 and 22. This may be the result of relatively high structural stability or probably due to the irregularity of structural changes with sodium exchange and varying soil solution concentration. Therefore calibration may not be necessary for the various soil ESP levels on these soils. It was expected that Lualualei Series would experience significant changes with soil ESP, the lack of sodium effect may be a result of ineffective equilibration with the leaching solutions or other experimental differences such as packing.

The effect of soil ESP on the mean $dEC_a/d\theta$ of the four soils is shown in Fig. 19 and the statistical analysis is presented in Table 34 in Appendix D. Apart from a generally rapid decline between ESP = 0

Table 20. Threshold water content (θ_t) of the selected soils at various soil ESP

	EXCHANGEABLE SODIUM PERCENTAGE						
SERIES	0.0	11.89	22.02	36.60	59.39	100.00	AVE
KAWAIHAE	16.43B */	15.60B	17.32B	15.73B	17.27B	20.63A	17.16
MOLOKAI	16.17AB	11.88B	13.49B	14.93B	14.38B	20.54A	15.23
LUALUALEI	20.62A	20.89A	14.15B	14.19B	19.54A	14.16B	17.26
KUKAIAU	33.55A	25.98BC	23.25C	26.87BC	25.00BC	30.00AB	27.44

*/Means followed by a common letter are not significantly different at the 5% level tested by the Duncan Multiple Range Test.

Table 21. -b/a values of the selected soil at various soil ESP

SERIES	EXCHANGEABLE SODIUM PERCENTAGE					
	0.0	11.89	22.02	36.60	59.39	100.00
KAWAIHAE	$\frac{-0.265}{1.613}$ */	$\frac{-0.188}{1.201}$	$\frac{-0.220}{1.269}$	$\frac{-0.187}{1.190}$	$\frac{-0.230}{1.330}$	$\frac{-0.422}{2.043}$
MOLOKAI	$\frac{-0.202}{1.249}$	$\frac{-0.139}{1.167}$	$\frac{-0.177}{1.310}$	$\frac{-0.185}{1.241}$	$\frac{-0.189}{1.313}$	$\frac{-0.394}{1.915}$
LUALUALEI	$\frac{-0.477}{2.315}$	$\frac{-0.310}{1.482}$	$\frac{-0.224}{1.583}$	$\frac{-0.245}{1.726}$	$\frac{-0.260}{1.332}$	$\frac{-0.203}{1.432}$
KUKAIAU	$\frac{-0.934}{2.783}$	$\frac{-0.166}{0.637}$	$\frac{-0.158}{0.679}$	$\frac{-0.199}{0.742}$	$\frac{-0.157}{0.628}$	$\frac{-0.342}{1.138}$

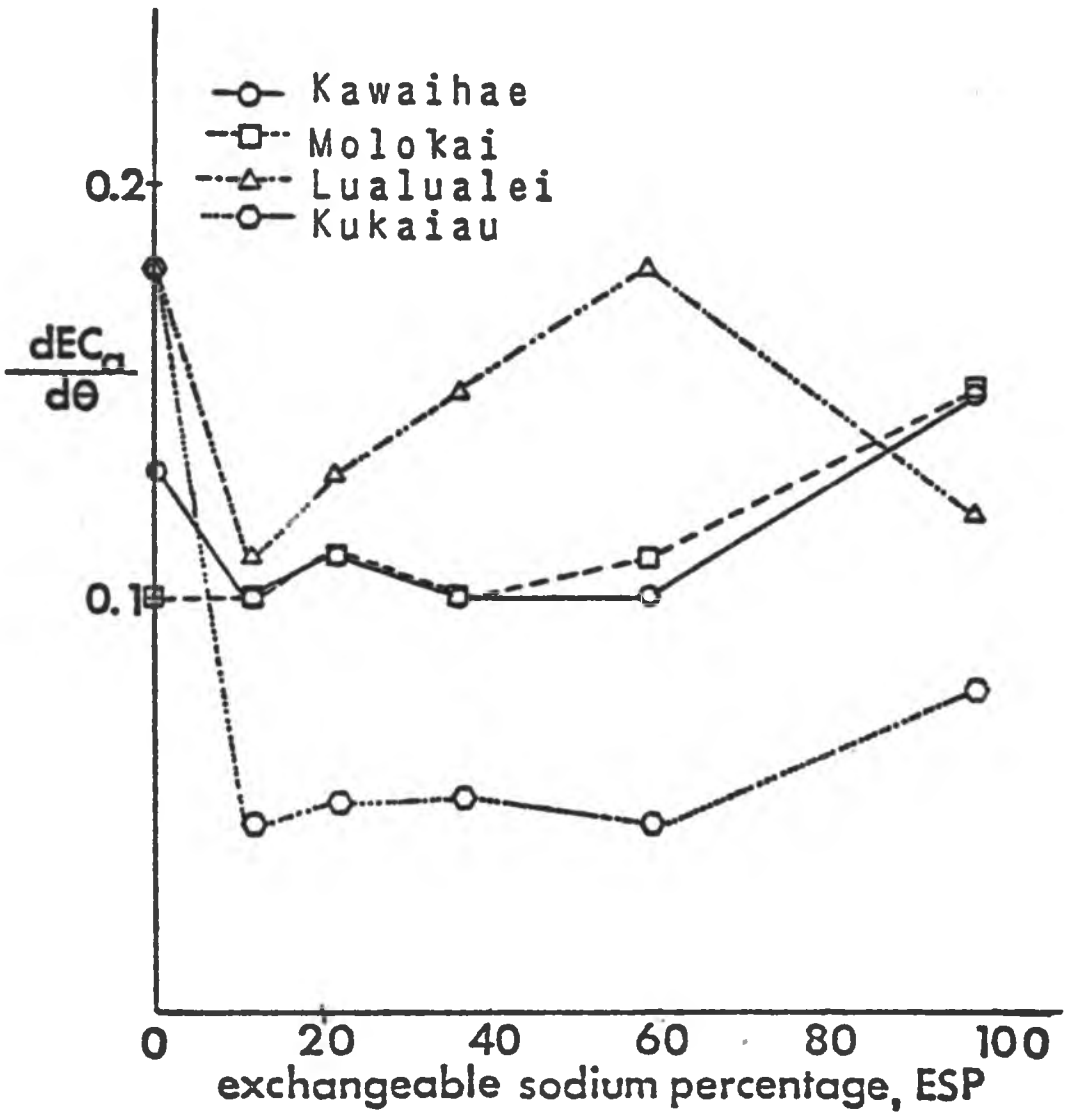
*/-b/a

Table 22. Correlation coefficient for the linear regression (r) between soil volumetric water content (θ) and transmission coefficient (T) of the selected soils at various soil ESP

	EXCHANGEABLE SODIUM PERCENTAGE						
SERIES	0.0	11.89	22.02	36.60	59.39	100.00	AVE
KAWAIHAE	0.90A */	0.89A	0.86AB	0.81B	0.88A	0.86AB	0.87
MOLOKAI	0.89BC	0.92AB	0.91ABC	0.97A	0.85C	0.93C	0.91
LUALUALEI	0.70C	0.88AB	0.74BC	0.71C	0.92A	0.74BC	0.78
KUKAIAU	0.90AB	0.96A	0.95A	0.95A	0.84B	0.93A	0.92

*/Means followed by a common letter are not significantly different at the 5% level tested by the Duncan Multiple Range Test.

Fig. 19. The effect of soil exchangeable sodium percentage (ESP) on the mean rate of change of bulk soil electrical conductivity with respect to soil volumetric water content ($dEC_a/d\theta$) for the four selected soils.


Kawaihae
Molokai
Lualualei
Kukaiau
0.2
0.1
$\frac{dEC_a}{d\theta}$
0
20
40
60
80
100
exchangeable sodium percentage, ESP

and ESP = 11.9 (except in Molokai Series), no consistent trend is observed. Except in Lualualei Series, values of $dEC_a/d\theta$ are fairly stable between the soil ESP values of 11.9 and 59.4 (confirmed by the statistical analysis) and this may be the result of the similarity of soil structure within this range.

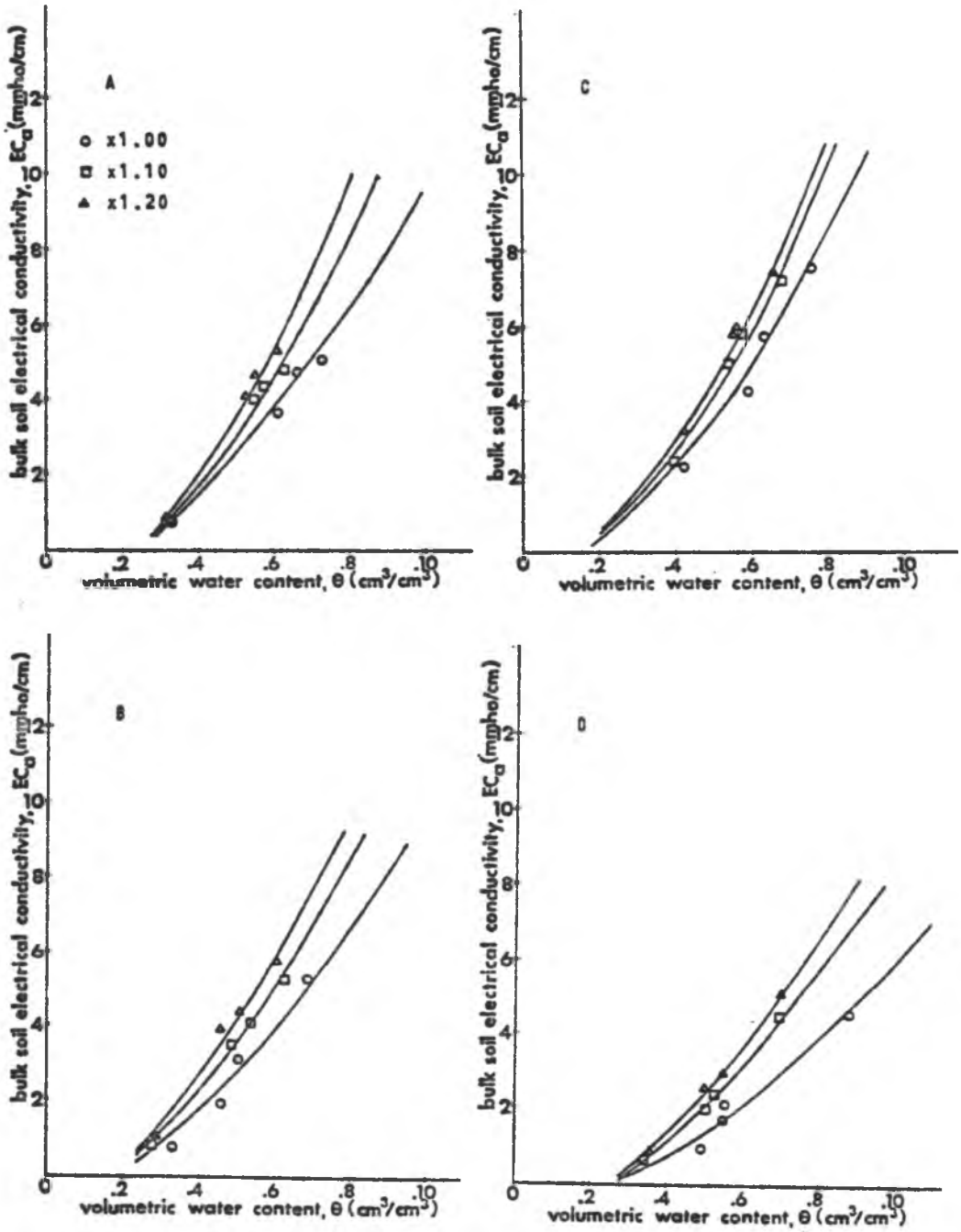
Effect of soil packing density on bulk electrical conductivity (EC_a)

As suggested previously, a change in bulk density in the core sample which resulted from structural failure affected EC_a measurements. Bulk density changes can also occur in the field due to a variety of other management conditions. Fig. 20 shows the impact of packing density on EC_a measurements on the four soils. The result shows that EC_a increases with increasing packing density and the effect is more significant at high soil water content (θ) than at low soil water content. In the Kukaiau Series, an increase in packing density from the range actually encountered in natural core (1.0) resulted in the greatest increase in EC_a when compared to the other three soils. The increase in EC_a in response to increasing packing density was probably due to the increase of mass per unit volume of soil that the Wenner Array could measure and/or the better direct physical contact between conducting particles such as sesquioxides thus improving the conductivity of the soil through the specific surface conductivity (EC_s).

In order to use bulk soil electrical conductivity to diagnose soil salinity and sodocity in the field where the field's bulk density is constantly changing through compaction resulting from heavy field

Fig. 20. Plots of bulk soil electrical conductivity, EC_a, vs. soil volumetric water content, θ, at three packing density levels for the four selected soils.

A. Kawaihae Series
B. Molokai Series
C. Lualualei Series
D. Kukaiau Series


A
o x1.00
□ x1.10
▲ x1.20
bulk soil electrical conductivity, EC_a (mmho/cm)
volumetric water content, θ (cm³/cm³)
B
C
D

traffic or field operations such as sub-soiling, the factor of packing density has to be accounted for. This is especially true if the diagnosis of such a field is done at a high soil water content (above field capacity).

To summarize the effects of soil variables on EC_a, generally speaking, bulk soil electrical conductivity increases with increasing soil volumetric content, soil solution concentration and packing density. The role of the soil exchangeable sodium percentage on bulk soil electrical conductivity is not clear and the higher bulk soil electrical conductivity possessed by the Ca-saturated soil is probably an artifact. The specific surface conductivity is a function of mineralogy and particle-size distribution of the soil. Soils dominated by montmorillonite possess comparatively higher specific surface conductivity and bulk soil electrical conductivity than those composed mainly of kaolinite and sesquioxides. On the other hand, the higher the clay content, the greater is the specific surface conductivity.

The Contribution of Specific Surface Conductivity to Bulk Soil Electrical Conductivity (EC_a)

The effect of frequency on electrical conductivity measurements, formation factor (F), iso-conductivity point (K_{iso}) and geometry factor (K)

The electrical conductivity of suspensions and supernatants was measured at frequencies of 1 KHZ and 85 HZ. An example of the frequency effect on measured electrical conductivity is given on the Na-montmorillonite B suspension shown in Table 23. The electrical

Table 23. The electrical conductivity of the 2.5% Na-montmorillonite B gel measured at two frequencies, i.e., 85 HZ and 1 KHZ

Normality of the equilibrating solution (NaCl)	Frequency	
	85 HZ	1 KHZ
	- - - (mmho/cm)	- - - -
0.1	10.01	10.11
0.08	8.37	8.55
0.04	4.60	4.65
0.02	2.64	2.68
0.01	1.51	1.54
0.001	0.35	0.35
0.0001	0.17	0.17
0.0000	0.16	0.17

conductivity readings at 1 KHZ were higher, though not significantly, than those determined at 85 HZ. At low electrical conductivity, the frequency effect became negligible. Weiler and Chaussidon (1968) also observed a small variation of the electrical conductivity of various cationic saturated montmorillonite suspensions as a function of frequency and they attributed this phenomenon to the alteration of the dielectric constant upon frequency change.

The effect of frequency on the formation factor (F) and iso-conductivity point (K_{iso}) is shown in Table 24. The formation factor of the various minerals were fairly uniform and they were in the range between 1.01 and 1.09. As for the iso-conductivity points, the range was much wider. In general, the standard clay minerals possessed much larger iso-conductivity points than the synthetic sesquioxides. The magnitude of the cation exchange capacity (CEC) of various minerals was positively related to the iso-conductivity point as reported by Dakshinamurti (1960), though the properties of each individual mineral could not be neglected. Generally speaking, within the range of frequency used here, the frequency effect on both formation constant and iso-conductivity point was not obvious especially in the synthetic sesquioxides. An example of the frequency effect on the formation factor and iso-conductivity point of the Na-montmorillonite B is presented in Figs. 21 and 22, respectively.

The frequency effect was relatively more pronounced on the geometry factor (K) as shown in Table 25. According to eq. (16), a small variation in the formation factor between the two frequencies would result in a difference in the geometry factor of the same frequency.

Table 24. Formation factor (F) and iso-conductivity point (K_{iso}) of various mineral suspensions (2.5%) at two frequencies

Mineral	Formation factor			Isoconductivity point		
	85 HZ	1 KHZ	Avg.	85 HZ	1 KHZ	Avg.
				- - - (mmho/cm)		- - -
Na-montmorillonite A	1.06	1.09	1.08	3.52	3.77	3.65
Ca-montmorillonite A	1.07	1.05	1.06	3.20	2.80	3.00
Na-montmorillonite B	1.14	1.11	1.13	3.52	3.20	3.36
Ca-montmorillonite B	1.09	1.07	1.08	3.40	3.44	3.42
Na-kaolinite	1.01	1.01	1.01	0.41	0.42	0.42
Ca-kaolinite	1.01	1.01	1.01	0.32	0.34	0.33
Na-halloysite	1.02	1.01	1.02	0.46	0.41	0.44
Ca-halloysite	1.01	1.02	1.02	0.40	0.36	0.38
Na-goethite (fine)	1.01	1.01	1.01	0.07	0.06	0.07
Ca-goethite (fine)	1.01	1.01	1.01	0.12	0.11	0.12
Na-goethite (coarse)	1.01	1.0	1.0	0.09	0.08	0.09
Ca-goethite (coarse)	1.01	1.01	1.01	0.09	0.09	0.09
Na-bayerite	1.01	1.01	1.01	0.02	0.03	0.03
Ca-bayerite	1.01	1.01	1.01	0.03	0.05	0.04
Na-hematite	1.01	1.01	1.01	0.09	0.09	0.09
Ca-hematite	1.01	1.01	1.01	0.12	0.14	0.13

Fig. 21. Electrical conductivity of interclay solution vs. electrical conductivity of 2.5% Na-montmorillonite B gel at two frequencies.

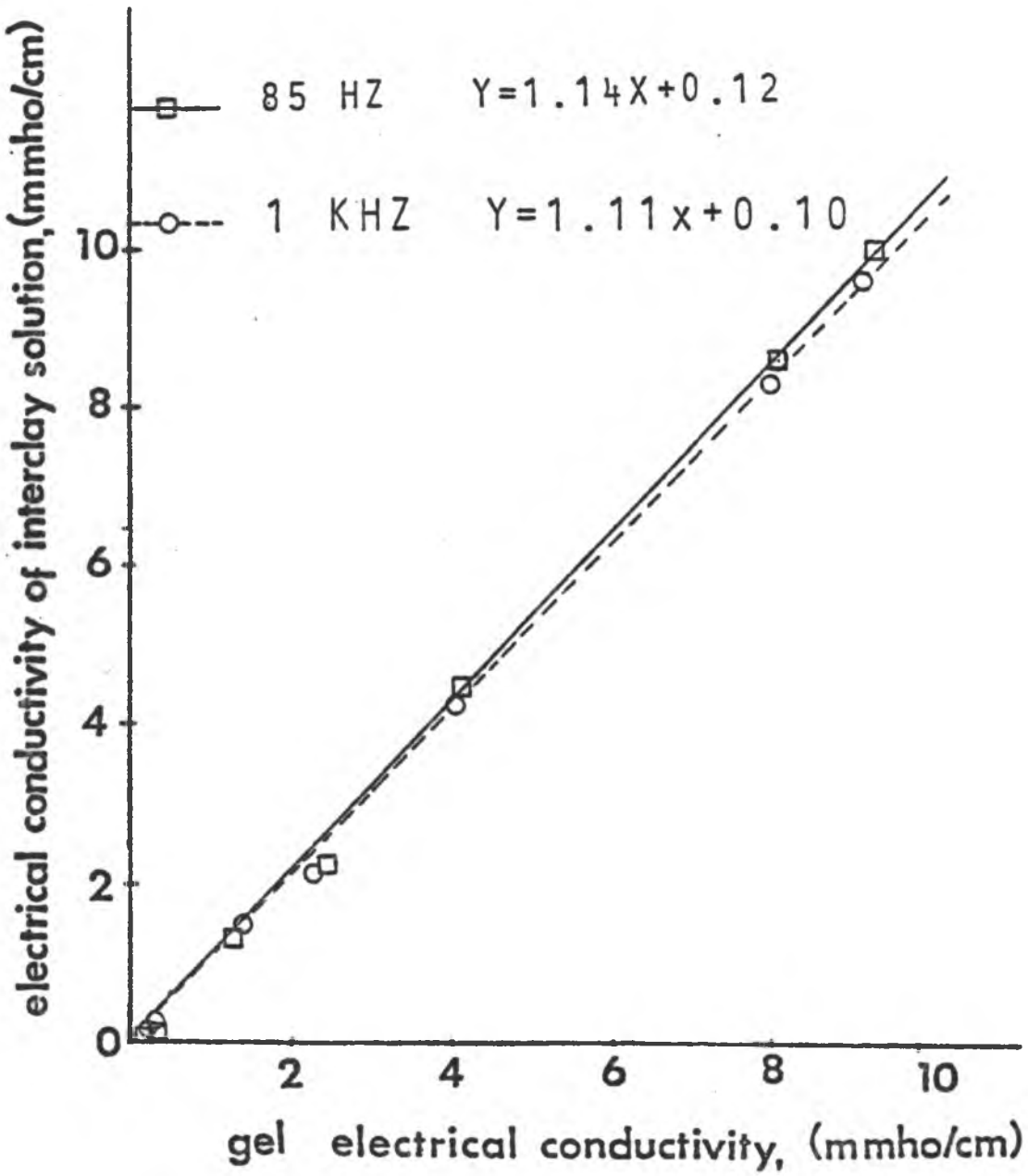

85 HZ Y=1.14X+0.12
1 KHZ Y=1.11x+0.10
electrical conductivity of interclay solution, (mmho/cm)
gel electrical conductivity, (mmho/cm)
0
2
4
6
8
10

Fig. 22. Difference between electrical conductivity of the 2.5% Na-montmorillonite B gel and interclay solution vs. the electrical conductivity of the interclay solution at two frequencies.

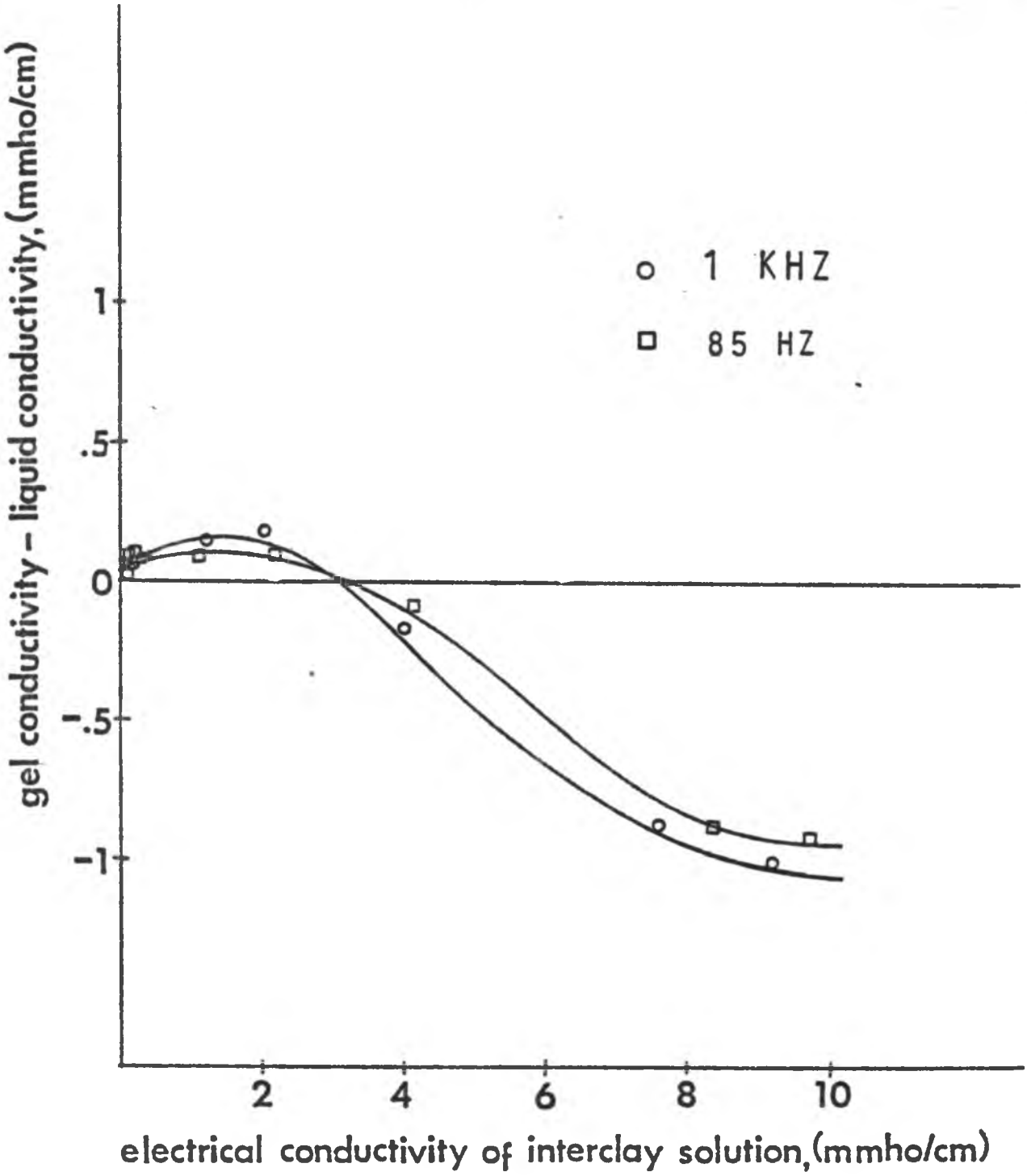

o 1 KHZ
□ 85 HZ
1
.5
0
-.5
-1
2
4
6
8
10
gel conductivity - liquid conductivity, (mmho/cm)
electrical conductivity of interclay solution, (mmho/cm)

Table 25. The geometry factor (K) of various mineral suspensions (2.5%) at two frequencies

Mineral	Geometry factor		
	85 HZ	1 KHZ	Avg.
Na-montmorillonite A	4.49	5.98	5.24
Ca-montmorillonite A	6.18	4.41	5.30
Na-montmorillonite B	9.78	7.69	8.74
Ca-montmorillonite B	7.60	5.91	6.76
Na-kaolinite	0.93	0.93	0.93
Ca-kaolinite	0.78	0.78	0.87
Na-halloysite	1.83	0.92	1.38
Ca-halloysite	0.92	1.84	1.38
Na-goethite (fine)	0.99	0.99	0.99
Ca-goethite (fine)	0.84	0.84	0.84
Na-goethite (coarse)	0.94	0.94	0.94
Ca-goethite (coarse)	1.10	1.10	1.10
Na-bayerite	0.86	0.86	0.86
Ca-bayerite	0.94	0.94	0.94
Na-hematite	1.63	1.63	1.63
Ca-hematite	2.07	2.07	2.07

For convenience, the mean formation factor, iso-conductivity point and geometry factor over the two frequencies were used to determine the surface conductance (K_S).

Surface conductance (K_S)

The "ideal" and "effective" surface conductance of various Ca and Na forms of standard clay minerals and synthetic sesquioxides were evaluated according to eqs. (14) and (15), respectively. The result is shown in Table 26. The "effective" surface conductance, which was evaluated by the iso-conductivity point theory, was much smaller than the "ideal" one in all the minerals under investigation. The "effective" surface conductance of Na-montmorillonite A obtained in this study was in good agreement with that of Shainberg and Levy (1974). In general, both the "ideal" and "effective" surface conductance of standard clay minerals were larger than those of the corresponding synthetic sesquioxides. Except in bayerite and goethite (fine), the "effective" surface conductance of the Na form was higher than that of the corresponding Ca form, though the trend was less obvious in kaolinite, goethite (coarse) and hematite. This can be explained by the Boltzmann equation:

$$n_+ = n_+^0 \exp - Z_i e^* w/kT$$

where

n_+ = average concentration of positive counter ions at a given point between negatively charged colloidal plates in the electrolyte medium

n_+^0 = concentration of these ions in the outside solution (electrolyte)

Z_i = charge of the counter ion

Table 26. "Ideal" and "effective" surface conductance of various minerals

Mineral	Surface conductance	
	"Ideal"	"Effective"
	----(x10^{-6} mmho)----	
Na-montmorillonite A	12.04	0.30
Ca-montmorillonite A	9.80	1.58
Na-montmorillonite B	11.82	5.20
Ca-montmorillonite B	10.71	2.35
Na-kaolinite	3.66	0.35
Ca-kaolinite	4.61	0.33
Na-halloysite	4.35	0.82
Ca-halloysite	7.00	0.75
Na-goethite (fine)	0.17	0.010
Ca-goethite (fine)	0.074	0.018
Na-goethite (coarse)	0.60	0.045
Ca-goethite (coarse)	0.56	0.033
Na-bayerite	1.75	0.041
Ca-bayerite	2.83	0.19
Na-hematite	2.93	0.14
Ca-hematite	3.00	0.11

e^* = electronic charge

w = potential at that given point between the plates

k = Boltzmann constant

T = absolute temperature

At a given point in the diffuse layer of a monoionic system, the concentration of monovalent Na^+ ions is greater than that of the divalent Ca^{++} ions. Since surface conductance is a measure of adsorbed ionic concentration and mobility, it is not surprising that Na-saturated minerals possess higher surface conductance values than those of the Ca counterparts. The opposite trend in bayerite and goethite (fine) can be attributed to the formation of additional charges through the process of specific adsorption of the divalent Ca^{++} ions on the surface of these two synthetic sesquioxides, therefore the overall surface charge was increased and in turn raised the surface conductance.

The effect of clay concentration in suspension on surface conductance has been widely known by investigators. Weiler and Chaussidon (1968) demonstrated that between a clay concentration of 12.02% and 49.85%, the surface conductance of the Na-Camp Berteau Montmorillonite ranged from 4.64×10^{-6} mmho to 2.73×10^{-6} mmho, with a maximum of 5.89×10^{-6} mmho at 20.98%. Cremers and Laudelout (1966) reported the dependence of the surface conductance of Na-Zettlite and Na-Boluvit Kaolinite on clay concentration. In this study, a 2.5% clay or mineral concentration was used because of the following reasons:

1.) Past experience revealed that beyond the clay concentration of 2.5%, the suspension would become so thick (viscous)

that the electrical conductivity measurements would be difficult to interpret. This is especially true in the case of Na-montmorillonite.

2.) The limited quantity of available synthetic sesquioxides made the use of higher sesquioxide concentration impossible.

3.) It was verified by the above authors that surface conductance increased with increasing clay concentration up to a particular point, beyond which a further increase in the concentration would result in a decrease in surface conductance. It is assumed that at a relatively low clay concentration of 2.5%, the surface conductance of various standard clay minerals and synthetic sesquioxides would be within the first half of the trend (increasing trend).

In order to explore item 3, a simple experiment was performed to study the effect of clay and sesquioxide concentration on surface conductance. The clay or sesquioxide concentration was 2.5%, 5.0% and 10% and the surface conductance was determined as previously at 85 HZ. The montmorillonite was not included because ample evidence from past data had demonstrated that the critical concentration (beyond which the surface conductance would decrease) of montmorillonite was well above 2.5%. On the other hand, due to the insufficient amount of synthetic sesquioxides such as goethite and hematite prepared, they were also excluded. The formation factor (F), geometry factor (K), iso-conductivity point (K_{iso}) of kaolinite,

halloysite and bayerite measured at the frequency of 85 HZ are shown in Table 27. Figure 23 shows the effect of clay or sesquioxide concentration on surface conductance (K_s).

The formation factor was greater at higher clay or sesquioxide concentration as had been reported by Shainberg and Levy (1968). However, their observation that the iso-conductivity point (K_{iso}) should be independent of the clay or sesquioxide concentration, was not conclusively supported here, although the values were close. The surface conductance (K_S) was larger at higher clay or sesquioxide concentration. Assuming that montmorillonite, goethite and hematite possess a similar trend as above, the overall magnitude of the surface conductance within the clay (sesquioxide) concentration of 0 to 10%, is in the following order:

montmorillonite > halloysite > kaolinite > hematite

bayerite > goethite (coarse) > goethite (fine)

Specific surface conductivity (EC_S)

The specific surface conductivity which was evaluated from the corresponding surface conductance by eq. (17), is shown in Table 28. The "ideal" specific surface conductivity was much greater in magnitude than the corresponding "effective" specific surface conductivity. The "effective" specific surface conductivity of the synthetic sesquioxides were much less than those of the similarly saturated standard clay minerals. Like the surface conductance, the specific surface conductivity is a function of clay or sesquioxide concentration. Weiler and Chaussidon (1968) obtained maximum specific surface conductivity values measured at 1 KHZ for various cationic saturated Camp-Berteau

Table 27. The effect of suspension concentration on iso-conductivity point, formation factor and geometry factor for kaolinite, halloysite and bayerite measured at 85 HZ

Mineral	Iso-conductivity point, K_{iso}			Formation factor, F			Geometry factor, K		
	2.5	5.0	10.0	2.5	5.0	10.0	2.5	5.0	10.0
	(mmho/cm - %)			(%)			(%)		
Na-kaolinite	0.42	0.48	0.52	1.01	1.03	1.06	0.93	1.43	1.31
Ca-kaolinite	0.32	0.36	0.42	1.01	1.03	1.06	0.78	1.38	1.52
Na-halloysite	0.46	0.57	0.54	1.02	1.05	1.12	1.83	2.46	2.69
Ca-halloysite	0.40	0.38	0.43	1.01	1.03	1.08	0.92	1.47	1.78
Na-bayerite	0.02	0.05	0.07	1.01	1.02	1.03	0.86	0.66	0.52
Ca-bayerite	0.03	0.07	0.09	1.01	1.01	1.03	0.94	0.57	0.70

Fig. 23. The effect of clay (sesquioxides) concentration in suspension on surface conductance for kaolinite, halloysite and bayerite measured at 85 HZ.

● Na-halloysite
○ Ca-halloysite
■ Na-kaolinite
□ Ca-kaolinite
▲ Na-bayerite
△ Ca-bayerite

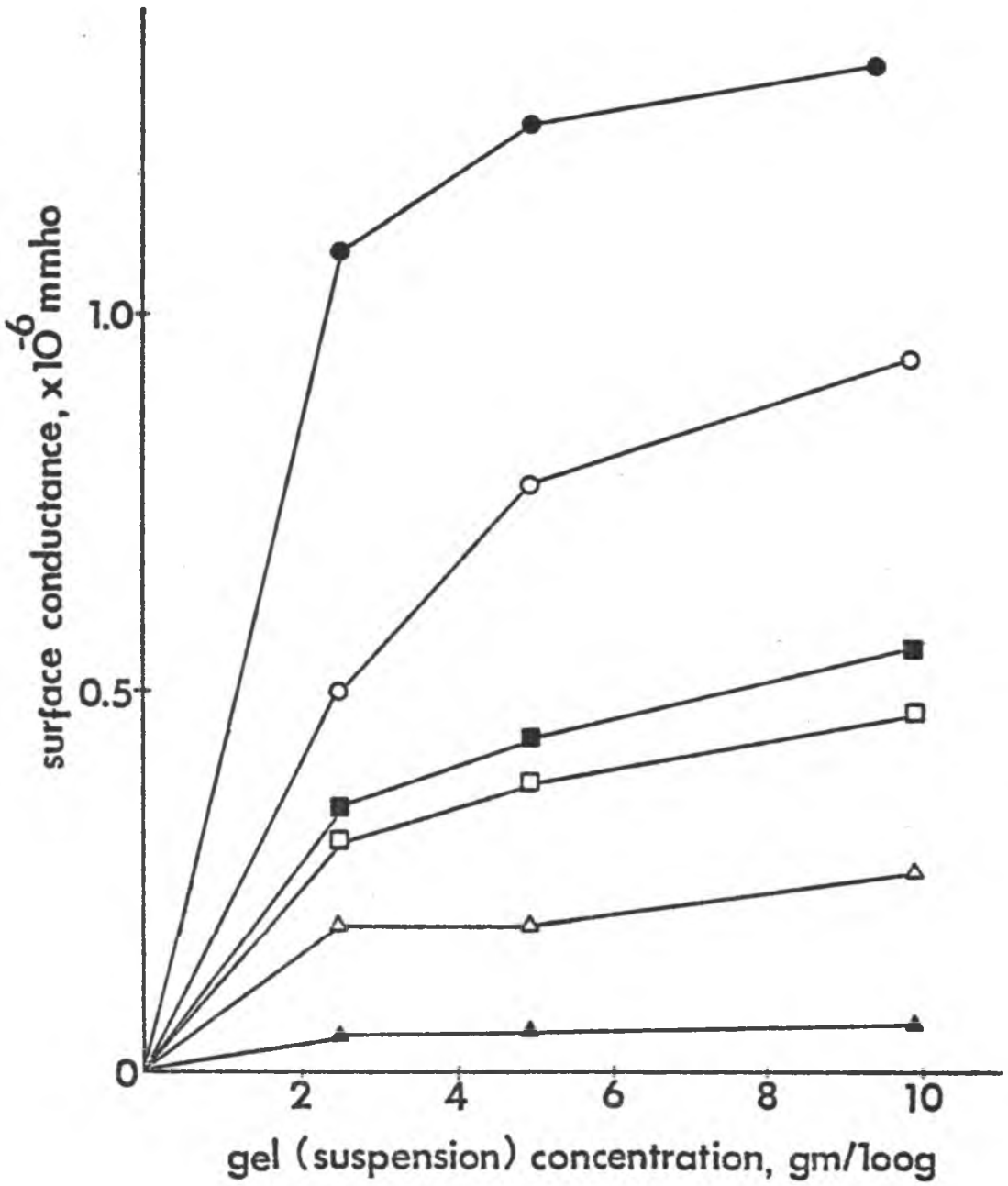

surface conductance, x10^-6 mmho
1.0
0.5
0
2
4
6
8
10
gel (suspension) concentration, gm/100g

Table 28. "Ideal" and "effective" specific surface conductivity of various minerals

Mineral	Specific surface conductivity	
	"Ideal"	"Effective"
	(mmho/cm)	
Na-montmorillonite A	29.77	8.16
Ca-montmorillonite A	41.73	6.73
Na-montmorillonite B	28.34	12.46
Ca-montmorillonite B	44.56	9.71
Na-kaolinite	1.71	0.16
Ca-kaolinite	1.72	0.12
Na-halloysite	1.37	0.26
Ca-halloysite	2.07	0.22
Na-goethite (fine)	0.64	0.036
Ca-goethite (fine)	0.25	0.060
Na-goethite (coarse)	0.66	0.049
Ca-goethite (coarse)	0.89	0.052
Na-bayerite	0.47	0.011
Ca-bayerite	0.23	0.015
Na-hematite	1.32	0.063
Ca-hematite	3.18	0.12

Montmorillonite by plotting EC_s vs. clay concentration. In the sodium system, with the clay concentration varying from 12.02 to 49.85%, the specific surface conductivity was evaluated to be between 39.4 mmho/cm and 23.20 mmho/cm and with the maximum of 38.8 mmho/cm at 32.54%. The dependence of specific surface conductivity of kaolinite, halloysite and bayerite on their suspension's concentration is shown in Fig. 24. Assuming the montmorillonite, goethite and hematite behaved similarly as above, therefore the comparison of the specific surface conductivity for the standard clay minerals and synthetic sesquioxides within the above concentration range (0 to 10%) is in the following order:

montmorillonite > halloysite > kaolinite > hematite

goethite (fine) > goethite (coarse) > bayerite

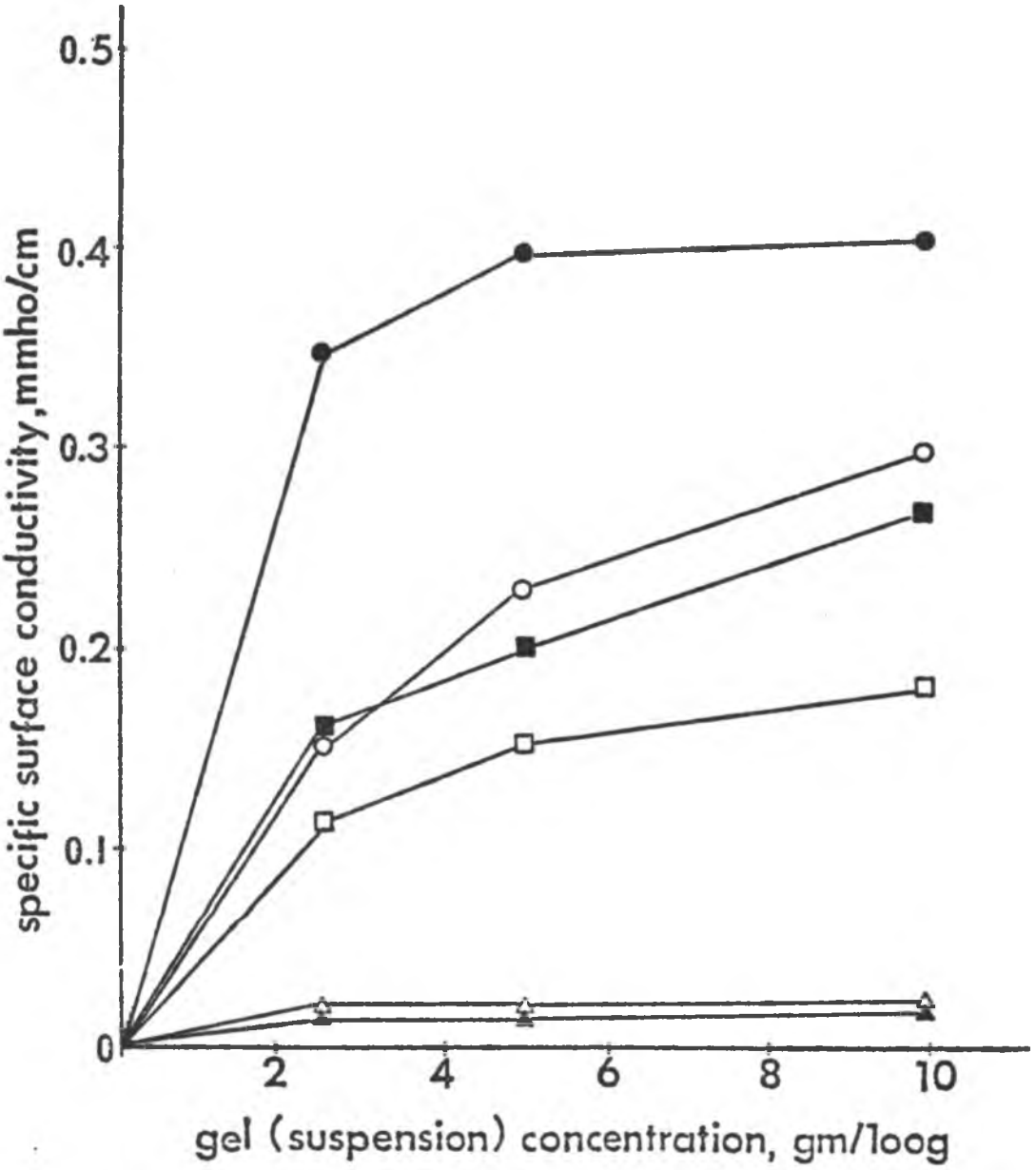
It would appear, therefore, that the charge density at the diffuse double layer is the primary factor affecting the specific surface conductivity and not the matrix's dielectric constant.

Relationship between the specific surface conductivity obtained from suspension and soil data

Even if the assumption that the mean specific surface conductivity of the soil is the weighted mean of the specific surface conductivity of its constituents is valid and the mineralogy of the soil is known, it is still not possible to establish a mathematical relationship between these two quantities. This is due to the difference in the matrix make-up between the bulk and suspension systems. In the bulk system, unlike the suspension system, most of the conducting channels are blocked, thus results in a lower surface conductance which in turn decreases the specific surface conductivity.

Fig. 24. The effect of clay (sesquioxides) concentration in suspension on specific surface conductivity for kaolinite, halloysite and bayerite measured at 85 HZ.

● Na-halloysite
○ Ca-halloysite
■ Na-kaolinite
□ Ca-kaolinite
▲ Na-bayerite
△ Ca-bayerite


0.5
0.4
0.3
0.2
0.1
0
specific surface conductivity, mmho/cm
2
4
6
8
10
gel (suspension) concentration, gm/100g

Qualitatively, however, the data derived from the suspension work show clearly that the contribution of the specific surface conductivity to bulk soil electrical conductivity depends on the mineralogical composition and the saturation status of the soil. For instance, if a soil is primarily montmorillonitic and heavily Na-saturated, the role of the specific surface conductivity in the bulk soil electrical conductivity will be highly important. On the other hand, soils dominated by sesquioxides such as bayerite, goethite and/or hematite, at all saturation possibilities, the contribution of the specific surface conductivity to the bulk soil electrical conductivity would not be significant.

SUMMARY AND CONCLUSIONS

The objectives of this study were:

1.) To investigate the effect of salt level, water content, exchangeable cations and soil bulk density on bulk soil electrical conductivity.

2.) To evaluate the impact of soil particle-size distribution and mineralogy through contributions to specific surface conductivity, on bulk soil electrical conductivity.

The bulk soil electrical conductivity increased with increasing liquid-phase electrolyte concentration (EC_w), soil volumetric water content (θ) and packing density. The effect of liquid-phase concentration and packing density on bulk soil electrical conductivity was less at low soil water content than at high soil-water content. Apart from the observation that Ca-saturated soils possessed a higher bulk soil electrical conductivity than others, the effect of soil exchangeable sodium percentage (ESP) on bulk soil electrical conductivity was far from clear. At the same time, a consistent trend between soil exchangeable sodium percentage and threshold water content (θ_t) or correlation coefficient (between transmission coefficient and soil volumetric water content) was not observed.

The rate of change of bulk soil electrical conductivity with respect to soil volumetric water content depended on liquid-phase concentration and soil volumetric water content. Among the four soils in this study, the mean $dEC_a/d\theta$ was in the following order:

Lualualei > Kawaihae ∿ Molokai > Kukaiau

The mean specific surface conductivity (EC_s) of soils depended on the particle-size distribution. The greater the content of clay-size particles, the larger was the specific surface conductivity. Among the four soils in this study, the order of the specific surface conductivity was as follows:

Lualualei > Molokai > Kawaihae > Kukaiau

The specific surface conductivity of minerals depended on the clay (sesquioxide) concentration in suspensions (gels) from which they were derived. The higher the mineral concentration, the greater was the specific surface conductivity. The specific surface conductivity among minerals was in the order of:

montmorillonite > halloysite > kaolinite > sesquioxides

Within individual minerals, the Na-form possessed a higher specific surface conductivity than the Ca-form in the standard clay minerals while a mixed trend was observed in the synthetic sesquioxides. The suspension work thus revealed that the contribution of specific surface conductivity to bulk soil electrical conductivity was mineral dependent. Under identical condition, soils with a montmorillonitic mineralogy possessed the highest specific surface conductivity while on the other extreme, those predominated by sesquioxides with the lowest. The mean specific surface conductivity obtained from the core sample for the four soils with a representative mineralogy also followed a similar trend.

APPENDIX

(A - F)

Appendix A

X-ray diffraction patterns for various synthetic sesquioxide

Fig. 25. X-ray diffraction pattern for the synthetic fine iron hydrous oxide (goethite).

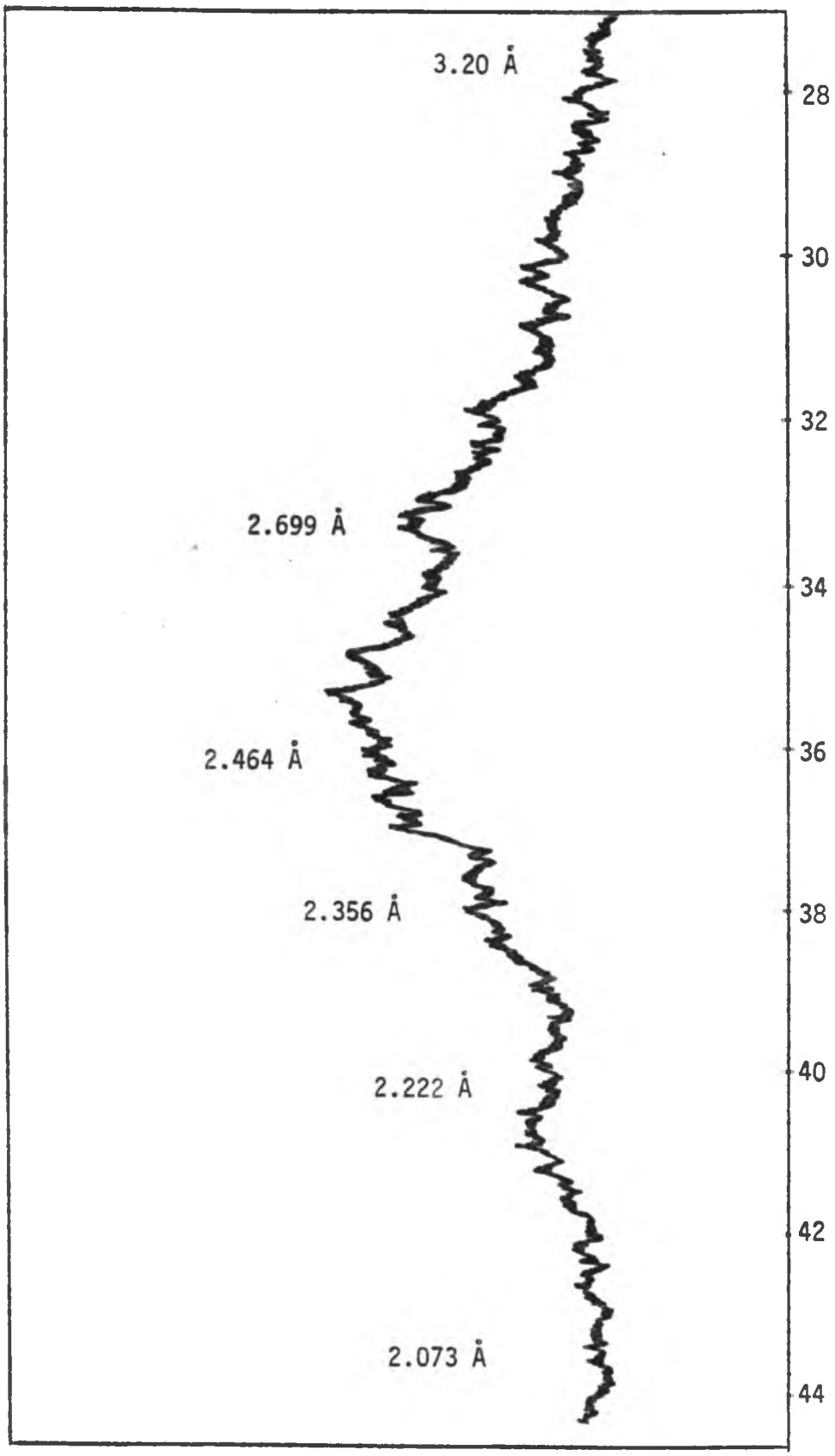

3.20 Å
2.699 Å
2.464 Å
2.356 Å
2.222 Å
2.073 Å
28
30
32
34
36
38
40
42
44

Fig. 26. X-ray diffraction pattern for the synthetic coarse iron hydrous oxide (goethite).

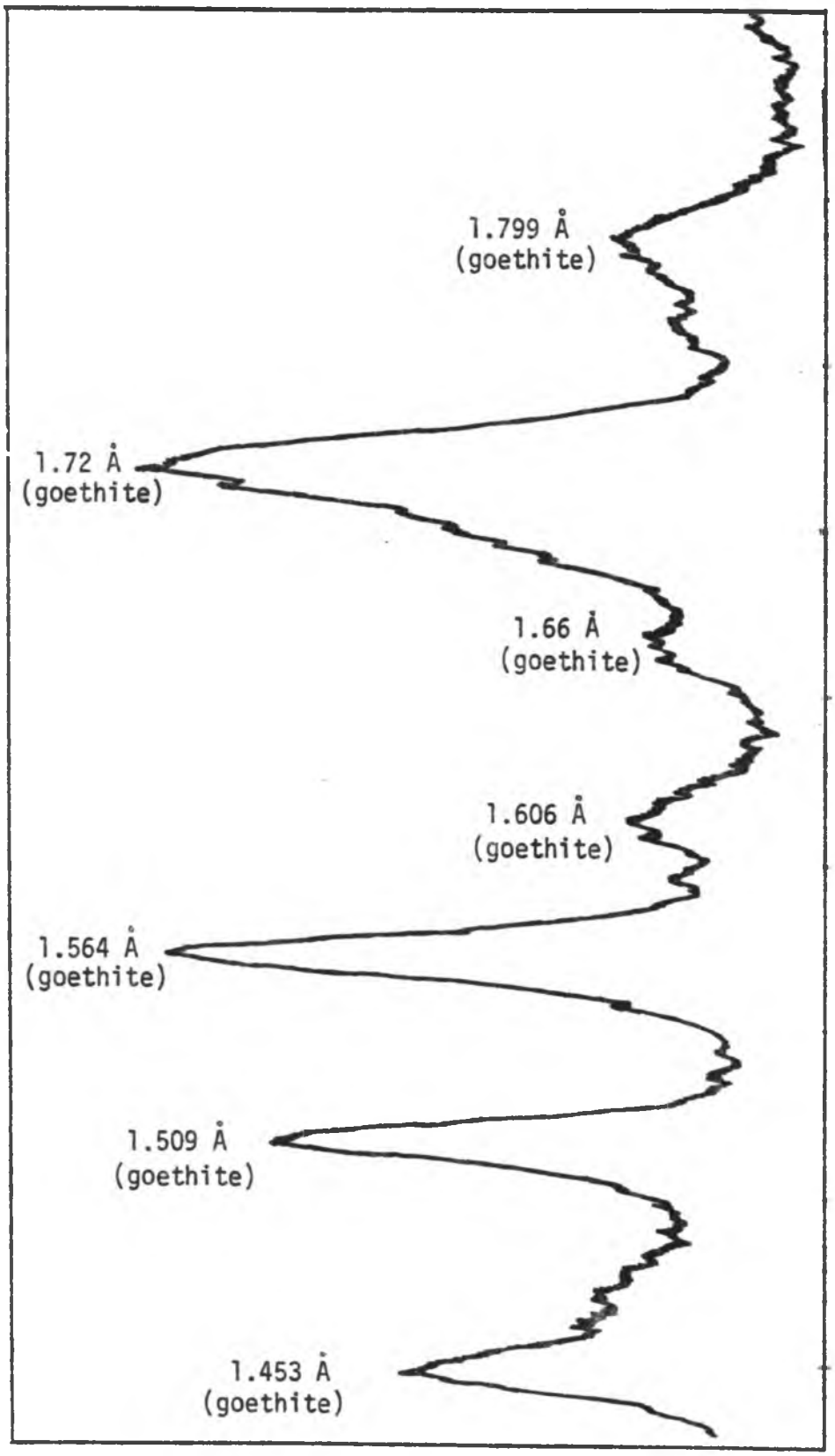

48
50
52
54
56
58
60
62
64
1.799 Å
(goethite)
1.72 Å
(goethite)
1.66 Å
(goethite)
1.606 Å
(goethite)
1.564 Å
(goethite)
1.509 Å
(goethite)
1.453 Å
(goethite)

Fig. 27. X-ray diffraction pattern for the synthetic iron oxide (hematite).

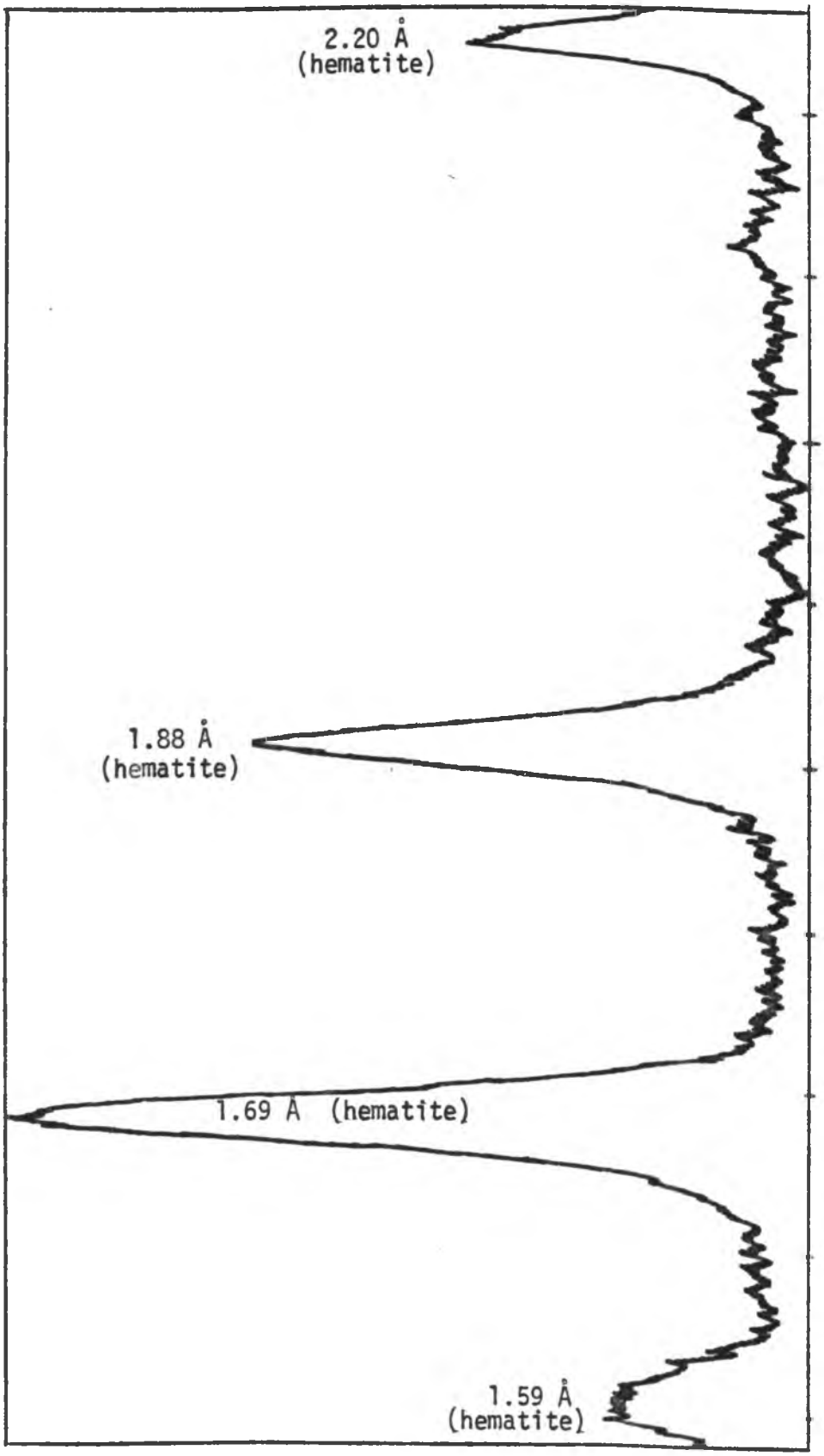
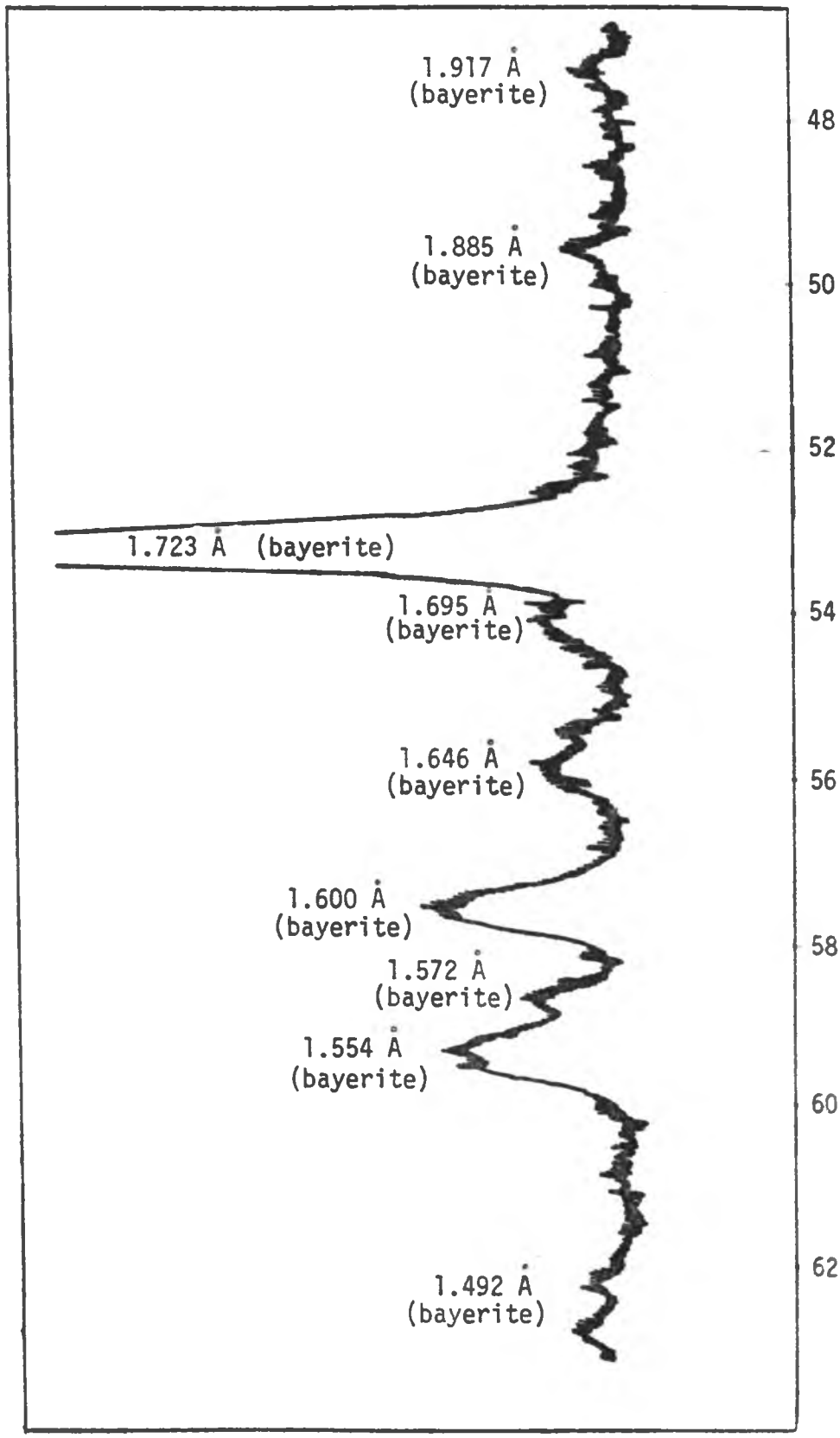

2.20 Å
(hematite)
1.88 Å
(hematite)
1.69 Å (hematite)
1.59 Å
(hematite)
42
44
46
48
50
52
54
56
58

Fig. 28. X-ray diffraction pattern for the synthetic aluminum hydroxide (gibbsite/bayerite).


1.917 Å
(bayerite)
1.885 Å
(bayerite)
1.723 Å (bayerite)
1.695 Å
(bayerite)
1.646 Å
(bayerite)
1.600 Å
(bayerite)
1.572 Å
(bayerite)
1.554 Å
(bayerite)
1.492 Å
(bayerite)
48
50
52
54
56
58
60
62

Appendix B

Table 29. Compositions of various equilibrating solutions for establishing soils to desired ESP and EC_w levels based on the U.S. Salinity Laboratory equation*/

EC_w	Exchangeable sodium percentage											
	0		11.9		22.0		36.6		59.4		100.0	
	Na	Ca	Na	Ca	Na	Ca	Na	Ca	Na	Ca	Na	Ca
4.0	0.0**/	40.0**/	26.23	13.77	34.16	5.84	38.18	1.82	39.69	0.31	40.0	0.0
8.0	0.0	80.0	43.01	36.99	61.25	18.75	73.29	6.71	78.76	1.24	80.0	0.0
12.0	0.0	120.0	56.39	63.61	84.39	35.61	105.96	14.04	117.25	2.75	120.0	0.0
20.0	0.0	200.0	78.08	121.92	123.61	76.39	165.69	34.31	192.58	7.42	200.0	0.0

*/ $ESP = \frac{100(-0.0126 + 0.01475SAR)}{1+(-0.0126 + 0.01475SAR)}$

**/Expressed in meq/1000ml of NaCl and $CaCl_2$, respectively.

Appendix C

Relationship between bulk soil electrical conductivity. EC_a, and soil exchangeable sodium percentage levels at different liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for the selected soils.

Table 30. Relationship between bulk soil electrical conductivity, EC_a, and soil exchangeable sodium percentage levels at different liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for Kawaihae Series: A. θ=0.30, B. θ=0.40, C. θ=0.50, D. θ=0.60

	EC w	EXCHANGEABLE SODIUM PERCENTAGE					
		0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
A	4.0	0.45A */	0.25BC	0.15BC	0.20BC	0.30AB	0.10C
	8.0	0.60A	0.55A	0.20B	0.30B	0.40AB	0.30B
	12.0	0.80A	0.70AB	0.40C	0.50BC	0.70AB	0.50BC
	20.0	1.05ABC	1.20AB	0.52C	0.70BC	1.45A	0.72BC
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC w	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
B	4.0	0.86A */	0.70AB	0.62B	0.60B	0.81AB	0.50B
	8.0	1.51A	1.14B	0.90B	1.00B	1.08B	1.16B
	12.0	1.78A	1.66AB	1.23C	1.45BC	1.58AB	1.53AB
	20.0	2.85A	2.77AB	2.16BC	2.15C	2.62AB	2.40ABC
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC w	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
C	4.0	1.32A */	1.20ABC	1.11BC	1.05C	1.34A	1.28AB
	8.0	2.58A	1.80B	1.72B	1.92B	2.08B	2.18AB
	12.0	2.91A	2.71AB	2.30C	2.52BC	2.77AB	2.91A
	20.0	4.82A	4.50AB	4.00BC	3.80C	4.07BC	4.54AB
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC w	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
D	4.0	1.88B */	1.71B	1.70B	1.54B	1.90B	2.32A
	8.0	3.70A	2.58C	2.70BC	2.76BC	3.32AB	3.32AB
	12.0	4.29AB	3.90BC	3.55C	3.72BC	4.27AB	4.54A
	20.0	6.56A	6.60AB	5.88BC	5.47C	5.82BC	7.15A

*/Means followed by a common letter are not significantly different at the 5% level tested by Duncan Multiple Range Test.

Table 31. Relationship between bulk soil electrical conductivity, EC_w, and soil exchangeable sodium percentage levels at different liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for Molokai Series: A. θ=0.30, B. θ=0.40, C. θ=0.50, D. θ=0.60

	EC$_w$	EXCHANGEABLE SODIUM PERCENTAGE					
		0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
A		*/					
	4.0	0.37A	0.20C	0.40A	0.25AB	0.35AB	0.35AB
	8.0	0.58AB	0.61AB	0.64A	0.40C	0.54AB	0.48BC
	12.0	0.71BC	0.82AB	0.82AB	0.51C	1.00A	0.62BC
	20.0	1.00BC	1.40A	1.28AB	0.97BC	1.43A	0.85C
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC$_w$	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
B		*/					
	4.0	0.73AB	0.50B	0.89A	0.58B	0.73AB	0.90A
	8.0	1.18A	1.18A	1.31A	0.86B	1.50A	1.21A
	12.0	1.61B	1.65B	1.81B	1.46B	2.20A	1.70B
	20.0	2.27B	2.78A	2.53AB	2.46AB	2.79A	2.23B
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC$_w$	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
C		*/					
	4.0	1.11BC	0.91C	1.40AB	0.94C	1.22ABC	1.51A
	8.0	1.90BC	1.81BC	2.06AB	1.60C	2.41A	2.22AB
	12.0	2.81BC	2.68BC	2.96BC	2.61C	3.55A	3.17AB
	20.0	3.82B	4.50A	4.18AB	4.20AB	4.51A	4.60A
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC$_w$	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
D		*/					
	4.0	1.51A	1.44B	1.92AB	1.38B	1.89B	2.30A
	8.0	2.71BC	2.68BC	2.35C	2.52C	3.45AB	3.54A
	12.0	4.22BC	3.89C	4.20BC	4.00C	5.00AB	5.20C
	20.0	5.71B	6.42B	6.10B	6.20B	6.50B	8.20A

*/Means followed by a common letter are not significantly different at the 5% level tested by the Duncan Multiple Range Test.

Table 32. Relationship between bulk soil electrical conductivity, EC_a, and soil exchangeable sodium percentage levels at different liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for Lualualei Series: A. θ=0.30, B. θ=0.40, C. θ=0.50, D. θ=0.60

	EC$_w$	EXCHANGEABLE SODIUM PERCENTAGE					
		0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
A		*/					
	4.0	0.708C	0.97AB	0.629C	0.51C	1.12A	0.70BC
	8.0	0.57ABC	1.10AB	0.833C	0.79C	1.21A	0.73C
	12.0	1.10BC	1.26ABC	1.00C	1.58A	1.42A	1.02C
	20.0	1.29BC	1.62AB	1.18C	1.76A	1.60AB	1.32BC
	EC$_w$	EXCHANGEABLE SODIUM PERCENTAGE					
		0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
B		*/					
	4.0	1.52A	1.52A	1.33AB	1.10B	1.50A	1.37A
	8.0	2.10A	1.91A	1.88AB	1.60B	1.87AB	1.62B
	12.0	2.45AB	2.20BC	2.10C	2.59A	2.30ABC	2.10C
	20.0	2.71ABC	2.92A	2.61BC	2.79AB	2.50C	2.60A
	EC$_w$	EXCHANGEABLE SODIUM PERCENTAGE					
		0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
C		*/					
	4.0	2.66A	2.16B	2.10B	2.91B	1.93B	2.07B
	8.0	3.41A	2.80AB	2.97AB	2.70B	2.71B	2.58B
	12.0	4.13A	3.40BC	3.40BC	3.87AB	3.51BC	3.24C
	20.0	5.09A	4.69A	4.50A	4.68A	3.90B	4.62A
	EC$_w$	EXCHANGEABLE SODIUM PERCENTAGE					
		0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
D		*/					
	4.0	3.77A	2.83B	2.95B	3.00B	2.39B	2.89B
	8.0	5.11A	3.80B	4.11B	4.04B	3.78B	3.68B
	12.0	6.33A	4.86B	4.97B	5.60AB	5.18B	4.70B
	20.0	8.12A	7.22ABC	6.68BC	7.67AB	6.33C	6.61BC

*/Means followed by a common letter are not significantly different at the 5% level tested by the Duncan Multiple Range Test.

Table 33. Relationship between bulk soil electrical conductivity, EC_a, and soil exchangeable sodium percentage levels at different liquid-phase electrical conductivity, EC_w, and soil volumetric water content, θ, for Kukaiau Series: A. θ=0.40, B. θ=0.50, C. θ=0.60, D. θ=0.70

	EC$_w$	EXCHANGEABLE SODIUM PERCENTAGE					
		0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
A		*/					
	4.0	0.46A	0.20B	0.18B	0.14B	0.14B	0.15B
	8.0	0.50A	0.30B	0.27B	0.30B	0.31B	0.32B
	12.0	0.7CA	0.56AB	0.36B	0.54AB	0.40B	0.69A
	20.0	1.51A	0.76B	0.72B	0.68B	0.62B	0.94B
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC$_w$	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
B		*/					
	4.0	0.95A	0.36B	0.35B	0.38B	0.35B	0.50B
	8.0	1.51A	0.55B	0.80B	0.70B	0.70B	0.91B
	12.0	2.71A	1.21B	1.06B	1.30B	0.92B	1.56B
	20.0	4.78A	1.70B	1.70B	1.51B	1.65B	2.32B
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC$_w$	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
C		*/					
	4.0	1.60A	0.56B	0.60B	0.61B	0.56B	1.00AB
	8.0	2.83A	0.90B	1.45B	1.20B	1.18B	1.64B
	12.0	5.22A	2.00B	1.87B	2.12B	1.60B	2.57B
	20.0	8.61A	2.90B	2.80B	2.55B	2.95B	3.86B
		EXCHANGEABLE SODIUM PERCENTAGE					
	EC$_w$	0.0	11.89	22.02	36.60	59.39	100.00
		MMHO/CM					
D		*/					
	4.0	2.90A	0.81B	0.90B	0.88B	0.80B	1.57AB
	8.0	4.92A	1.40B	2.20B	1.78B	1.75B	2.55B
	12.0	8.30A	2.90B	2.80B	3.10B	2.51B	3.90B
	20.0	12.70A	4.32B	4.20B	3.80B	4.48B	6.60B

*/Means followed by a common letter are not significantly different at the 5% level tested by the Duncan Multiple Range Test.

Appendix D

Table 34. The effect of soil ESP on the mean $dEC_a/d\theta$ for the selected soils

	EXCHANGEABLE SODIUM PERCENTAGE						
SERIES	0.0	11.89	22.02	36.60	59.39	100.00	AVE
KAWAIHAE	0.13AB */	0.10B	0.11B	0.10B	0.10B	0.15A	0.12
MOLOKAI	0.10B	0.10B	0.11B	0.10B	0.11B	0.15A	0.11
LUALUALEI	0.18A	0.11B	0.13B	0.15AB	0.18A	0.12B	0.15
KUKAIAU	0.18A	0.05B	0.05B	0.05B	0.05B	0.08B	0.08

*/Means followed by a common letter are not significantly different at the 5% level tested by the Duncan Multiple Range Test.

Appendix E

Fig. 29. Effects of core differences and swelling on the bulk soil electrical conductivity of Lualualei Series.

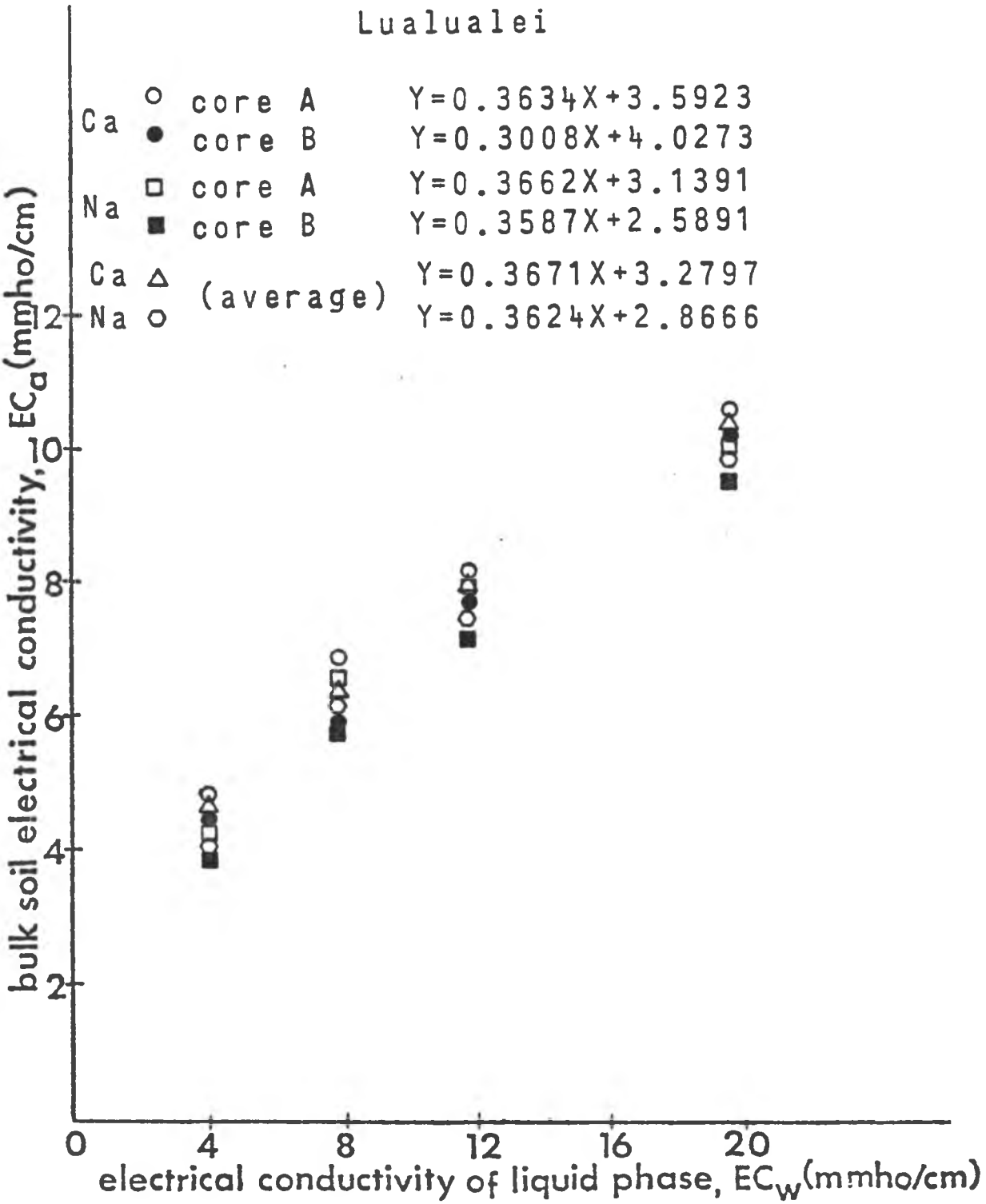
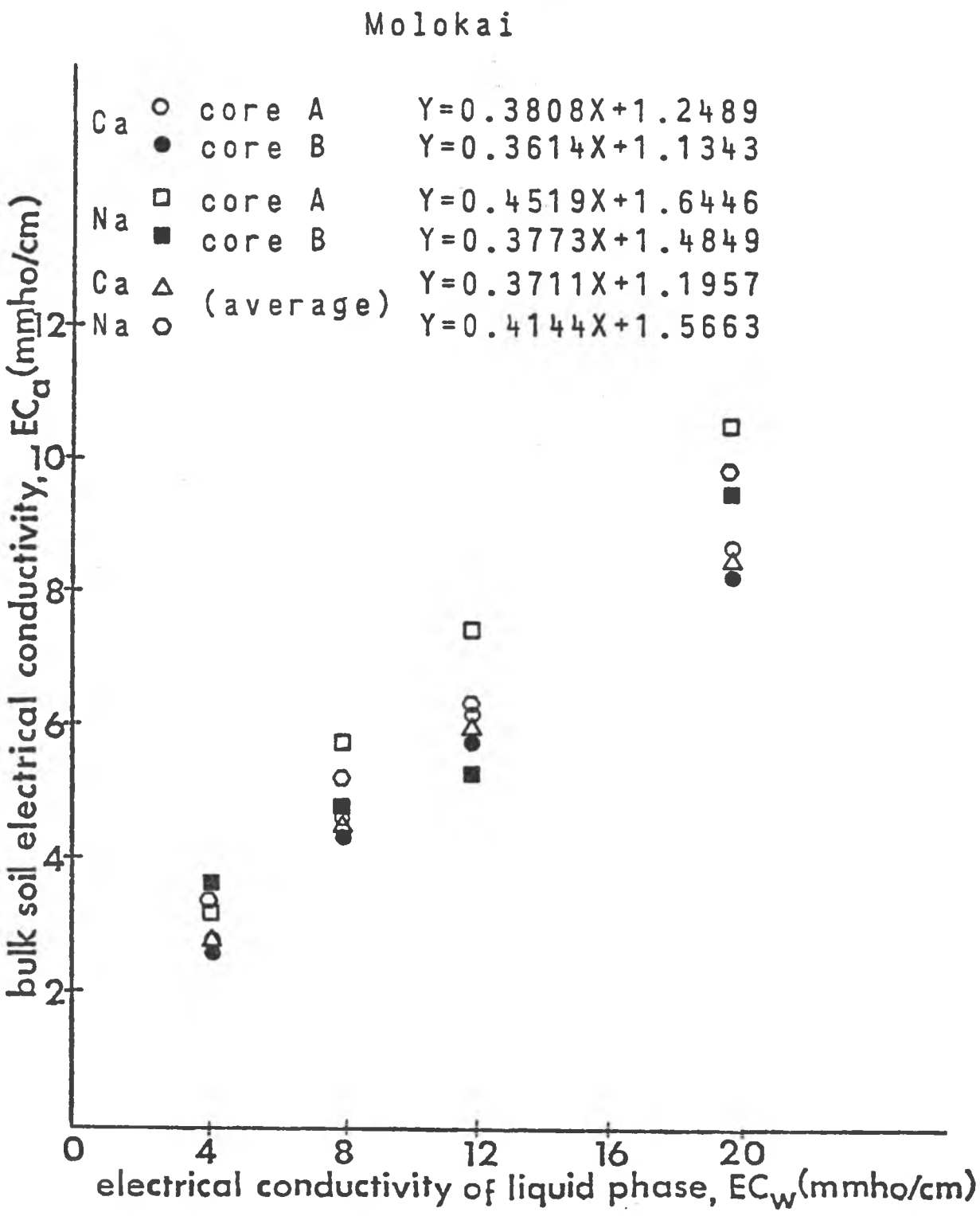

Lualualei
Ca ○ core A Y=0.3634X+3.5923
● core B Y=0.3008X+4.0273
Na □ core A Y=0.3662X+3.1391
■ core B Y=0.3587X+2.5891
Ca △ (average) Y=0.3671X+3.2797
Na ○ Y=0.3624X+2.8666
bulk soil electrical conductivity, ECa (mmho/cm)
2
4
6
8
10
12
0
4
8
12
16
20
electrical conductivity of liquid phase, ECw (mmho/cm)

Fig. 30. Effects of core differences and swelling on the bulk soil electrical conductivity of Molokai Series.


Molokai
Ca ○ core A Y=0.3808X+1.2489
● core B Y=0.3614X+1.1343
Na □ core A Y=0.4519X+1.6446
■ core B Y=0.3773X+1.4849
Ca △ (average) Y=0.3711X+1.1957
Na ○ Y=0.4144X+1.5663
bulk soil electrical conductivity, EC_a (mmho/cm)
0
2
4
6
8
10
12
0
4
8
12
16
20
electrical conductivity of liquid phase, EC_w (mmho/cm)

Appendix F

Sample calculation of surface conductance and specific surface conductivity

1. Calculation of surface conductance (K_s) of minerals

Example: Na-kaolinite

a. "Ideal" surface conductance

The "ideal" surface conductance is calculated by eq. (14):

$$K_s = L \times d$$

where

L = ionic equivalent conductivity at infinite dilution for Na^+

= 50.11 $cm^2\ eq^{-1}$ mho at 25°C

d = charge density of the mineral = CEC/sp. surface area

$$= \frac{3.43\ meq/100g}{47 \times 10^4\ cm^2/g} = 7.30 \times 10^{-11}\ eq/cm^2$$

Therefore, $K_s = 50.11 \times 7.30 \times 10^{-11} = \underline{3.65 \times 10^{-6}\ mmho}$

b. "Effective" surface conductivity

The "effective" surface conductance is calculated by eq. (15):

$$K_s = \frac{(K_{iso})(K)}{(P_p)(S)}$$

where

K_{iso} = average iso-conductivity point = 0.42 mmho/cm

K = average geometry factor = 0.93

P_p = particle density = 2.35 g/cm^3

S = specific surface area = 47×10^4 cm/g

Therefore, $K_s = \frac{(0.42)(0.93)}{(2.35)(47 \times 10^4)} = \underline{0.35 \times 10^{-6}\ mmho}$

2. Calculation of specific surface conductivity (EC_S) of minerals

Example: Na-kaolinite

a. "Ideal" specific surface conductivity

The "ideal" specific surface conductivity is evaluated by eq. (17):

$$EC_S = (4)(K_S)/(\pi)(a)$$

where

K_S = "ideal" surface conductance = 3.66×10^{-6} mmho

a = average effective radius = 27.2×10^{-9} m or 27.2×10^{-7} cm

Therefore, $EC_S = (4)(3.66 \times 10^{-6})/(\pi)(27.2 \times 10^{-7})$

$= \underline{1.71 \text{ mmho/cm}}$

b. "Effective" specific surface conductivity

The "effective" specific surface conductivity is evaluated by the same equation, i.e. eq. (17):

$$EC_S = (4)(K_S)/(\pi)(a)$$

where

K_S = "effective" surface conductance = 0.35×10^{-6} mmho

a = average effective radius = 27.2×10^{-9} m or 27.2×10^{-7} cm

Therefore, $EC_S = (4)(0.35 \times 10^{-6})/(\pi)(27.2 \times 10^{-7})$

$= \underline{0.16 \text{ mmho/cm}}$

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